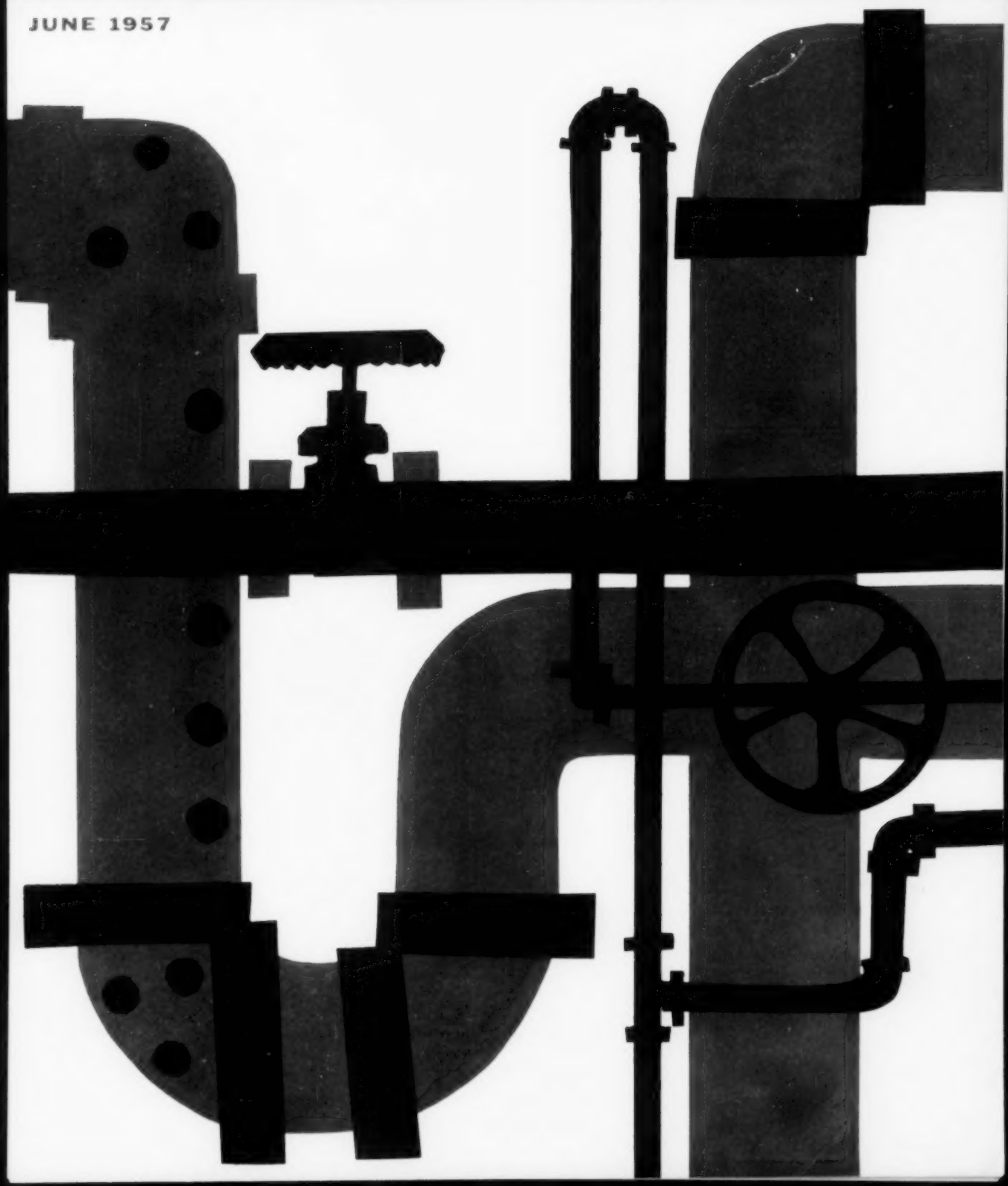
JOURNAL OF

METALS

JUNE 1957



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JUNE 1957

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COVER

"Treatment of ores by wet processes" is Webster's definition of hydrometallurgy, and when translated through the perceptive eye of the artist, you have this month's cover, done by Irene Trivas. For the latest articles of interest in this field—with the accent on uranium—turn to p. 745.

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Published the first day of each month by the American Institute of Mining, Metallurgical and Petroleum Engineers, Inc., 29 West 39th Street, New York 18, N. Y. Telephone: PEnnsylvania 6-9220. Subscription $8 per year for non-AIME members in United States and North, South, and Central America; $10, foreign; $6 for AIME members, or $4 additional in combination with a subscription to "Mining Engineering" or "Journal of Petroleum Technology." Single copies, 75 cents; single copies foreign, $1.00; special issues, $1.50. . . The AIME is not responsible for any statement made or opinion expressed in its publications. . . Copyright 1957 by the American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc. Registered cable address, AIME New York. . . Indexed in Engineering Index, Industrial Arts Index, and Chemical Abstracts. . . Second class mail privileges authorized at New York, N. Y., and additional entry established at Manchester, N. H. Number of copies of this issue 10,000.

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(*Continued on page 728*)

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(Continued from page 726)

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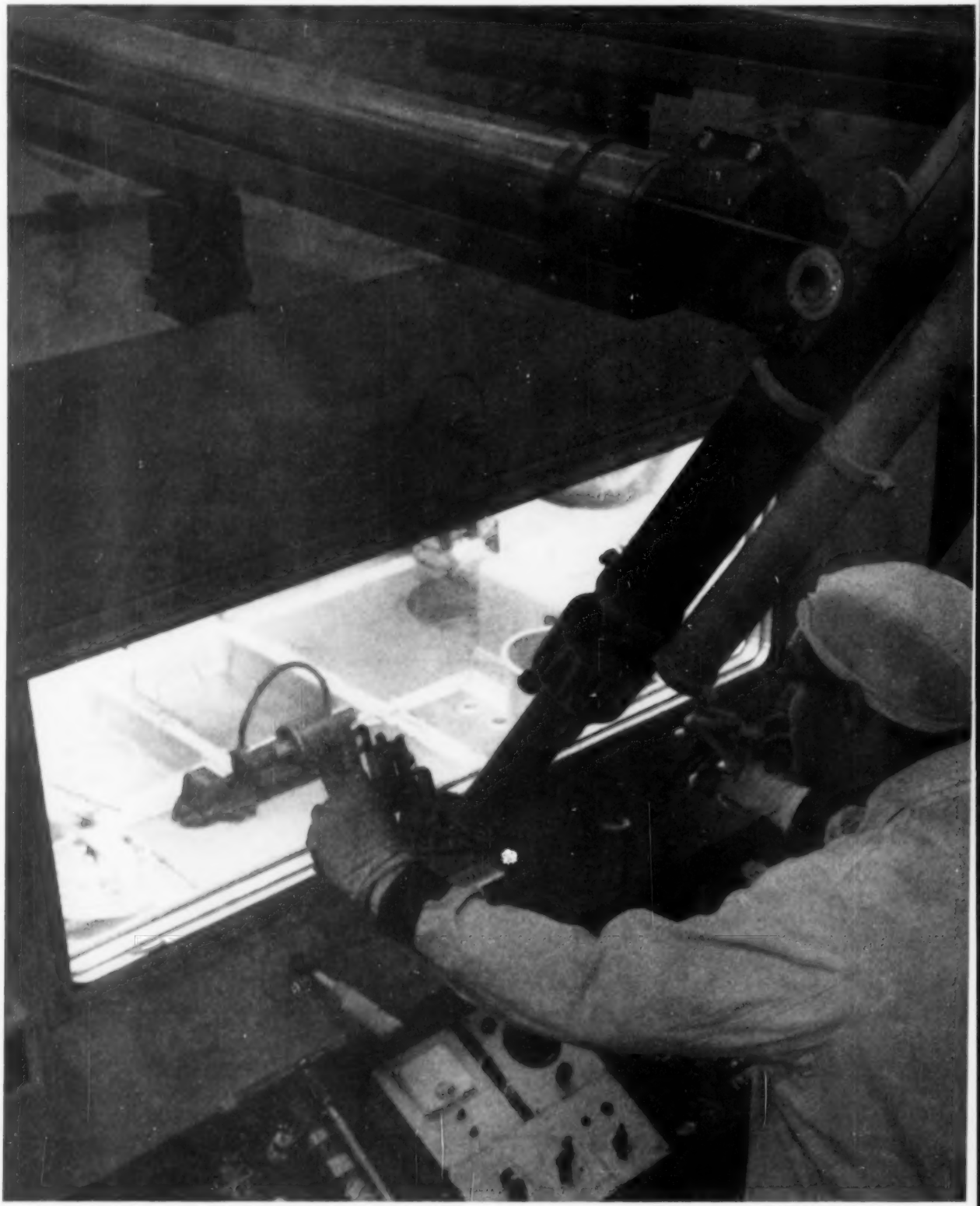
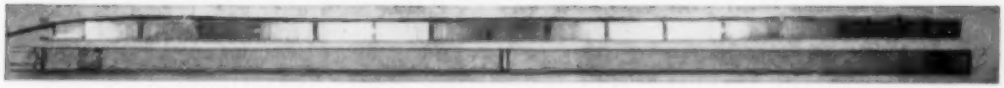
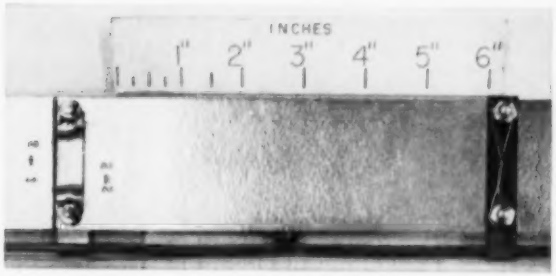


Fred Bingman, Metallographer, prepares metallographic specimens of irradiated materials by remote operation inside a shielded metallographic facility in the Bettis Atomic Power Division hot lab.

An Experimental Fuel Study of Uranium Alloys





A typical test array of instrumented uranium alloy fuel plates.

At Bettis Atomic Power Division laboratories, engineers and scientists are conducting basic research in the field of solid state physics and metallurgy to determine the behavior of nuclear materials under actual reactor conditions.

The experimental fuel plates shown on this page represent the initial step in a study of the temperature dependence of fuel materials to fission gas induced volume changes. These plates on an uranium-niobium alloy have been fabricated with thermocouples in the interior of the plates for constant temperature monitoring. The fuel enrichment is varied to provide the range of fuel temperature and fissioning rates of interest. The samples are being irradiated in a high temperature-high pressure recirculating water system at the NRX reactor site of Atomic Energy of Canada, Ltd., at Chalk River, Canada. The experiment will provide, in addition to data on fuel volume changes, information on neutron induced phase transformation kinetics and crystallographic changes.

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Extraction and Refining of the Rarer Metals, *Institution of Mining and Metallurgy*, 44 Portland Place, London W.1., England, 444 pp., $8.50, 1957.—This volume presents the proceedings of a symposium on extraction metallurgy of the less common metals, held in London in 1956. The proceedings include 22 papers, with discussions, devoted to such topics as purification by solvent extraction; recovery and concentration of uranium; chlorination of wolframite, vanadinite and chromite; processes for producing pure niobium; and the manufacture of hafnium-free zirconium. References accompany the papers. •

Molybdenum, by L. Northcott, *Academic Press Inc.*, 111 Fifth Ave., New York 3, N. Y., 222 pp., $6.80, 1956.—This monograph, No. 5 in the Metallurgy of the Rarer Metals Series, is an up-to-date study of the physical metallurgy and applications of molybdenum-rich alloys, with special emphasis given to problems involved in the low-oxidation resistance of the metal, embrittlement at low temperatures, and joining. •

Dunod Metallurgical Handbook, by R. Cazaud, *Dunod*, 92 rue Bonaparte, Paris 6e, France, in two volumes at approx. $1.38 each, 1957.—The 66th edition of this handbook is augmented by material on foundry and forging techniques, rolling mills, and general aspects of ferrous metallurgy. The contents are developed, under general categories, into a detailed treatment of specific problems and properties of alloys and metals.

Atomic Energy Applications with Reference to Underdeveloped Countries, by Bruce C. Netschert and Sam H. Schurr, *Johns Hopkins Press*, Baltimore 18, Md., 144 pp., $2.00, 1957.—This preliminary survey examines the technical, economic, and social problems regarding nonmilitary applications of atomic energy, suggests the necessary conditions for successful utilization, and indicates current and planned activities in international cooperation for bringing the benefits of atomic energy to underdeveloped countries. Among the applications discussed are uses of nuclear energy for power generation, heating for both residential and industrial purposes, radiation proc-

(*Continued on page 737*)

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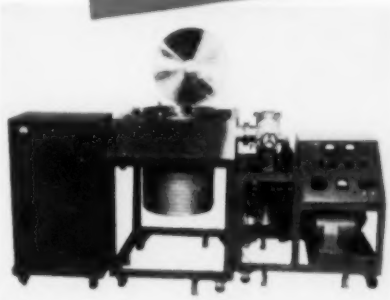

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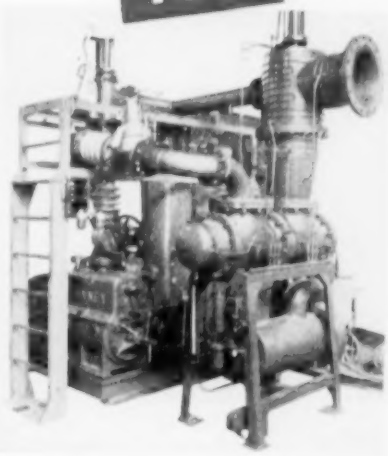

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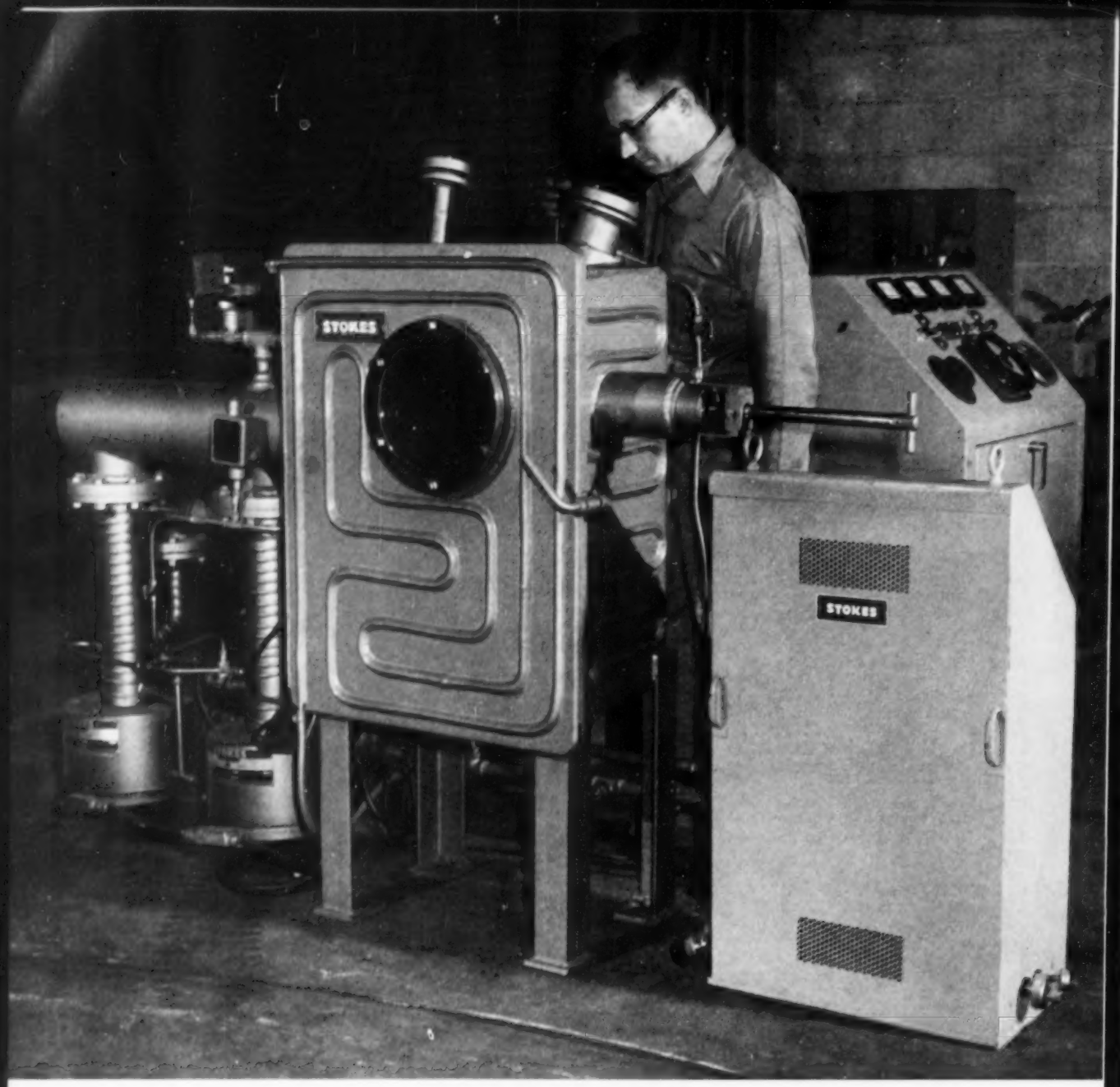
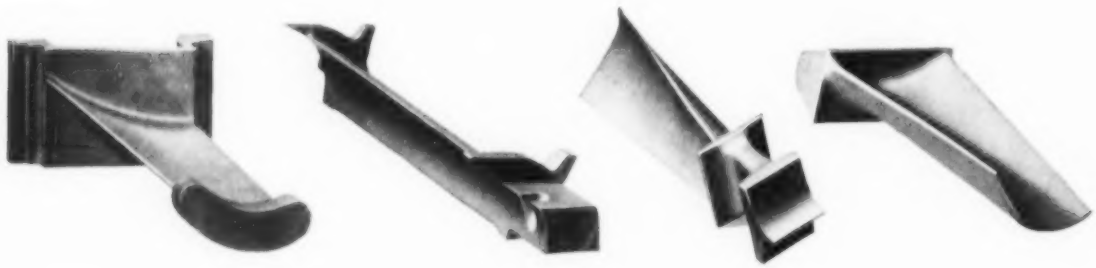


Typical precision castings which Austenal, Inc., Microcast Division, plans to produce with new Stokes Model 437-520 vacuum furnaces.



Here's a Really New Vacuum Furnace

for "all-out" production of precision castings

Stokes precision casting furnaces—capable of melting and pouring single casts of up to 30 pounds, under vacuums as low as 1 micron or less—are custom-designed and engineered to incorporate many operating features specially requested by precision casters. Units are in operation with charging and mold locks for semi-continuous production.

This low-cost "package" unit:

- pours smoothly... has a manually-operated tilting mechanism that operates easily.
- has good visibility . . . operator watches pour closely through 3-inch diameter shuttered sight glass.
- is easily operated . . . efficiently grouped controls cut operator's movements. Popular tandem units are operated by one man.
- can be set up for repetitive pre-determined melting and pouring cycles . . . interlocked, fail-safe controls permit operation by a normally skilled workman.
- provides accurate control over pouring temperatures . . . regularity of heat cycles cuts gage-watching time.
- takes up little floor space . . . measures 6'10" wide, 7'3" deep.

Others are taking advantage of Stokes advanced vacuum furnace technology in induction and arc melting, heat-treating and sintering. Isn't it time for you to contact Stokes for a discussion of your own profit-making opportunities?

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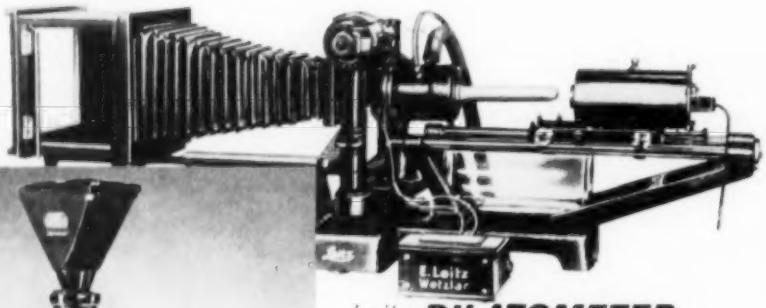

Leitz **DILATOMETER**

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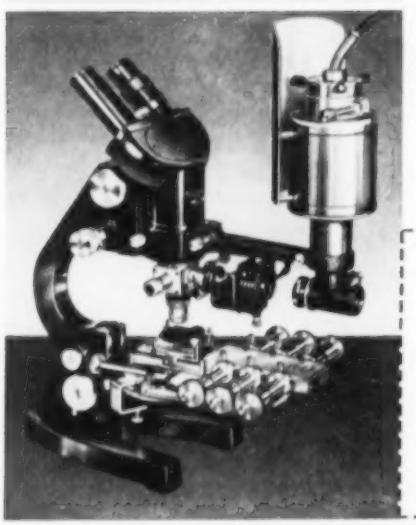
Researchers consider dilatometric analysis the most sensitive and reliable method for precise determination of the expansion coefficient of metals, alloys, etc. The *DILATOMETER* records volume changes in relation to its own temperature (absolute curve), yielding data from which the expansion coefficient may be determined.

Leitz **METALLUX** *microscope*

for easier, quicker metallography

Metallography is easier with the METALLUX—unobstructed upright stage, inclined eyepieces, unique quintuple nosepiece, built-in light and low-position controls for relaxed operation. Accessory equipment available for phase contrast, material testing and photography.



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Engineered specifically for coal-petrographic investigation, including examination by polarized or ordinary light, quantitative analysis and microscopic measurement. Fusain analysis readily accomplished by coal slide-comparison eyepiece with revolving disc.

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Books

(*Continued from page 733*)

essing, and use of radioisotopes in industry, agriculture, medicine, and general research. •

First Helper's Manual, *The Dolomitic Refractories Assn.*, 1279 W. Third St., Cleveland 13, Ohio, 79 pp., $3.00, 1957.—This text on practical open hearth steelmaking, written by the staff of Basic Inc., contains chapters on the open hearth plant, the open hearth furnace, raw materials, basic process chemistry, making a heat of steel, and furnace maintenance. Also included are appendices containing analyses of deoxidizers, alloying additions, refractories, and nonmetallic raw materials. •

Engineering Enrollment in the United States, ed. by Norman N. Barish, *New York University Press*, Washington Square, New York 3, N. Y., 226 pp., $7.50, 1957.—This volume presents basic statistics on enrollment trends in engineering education with suggestions concerning future qualitative and quantitative needs. In addition to sections on aeronautical, ceramic, chemical, geological, metallurgical, and mining engineering, a chapter on engineering training in the USSR is included. •

The Procedure Handbook of Arc Welding Design and Practice, *The Lincoln Electric Co.*, Cleveland 17, Ohio, 1300 pp., $3.00, 1957.—The 11th edition of this reference work has been revised and modernized and includes over 1100 illustrations, pictures, and charts. Contents cover all phases of arc welding from history to structural design, applications, and manufacturing cost data, and are divided into eight sections. An alphabetical index is also provided.

Proceedings of the High Temperature Symposium held last year on the University of California campus at Berkeley are available from the Public Relations Dept., *Stanford Research Institute*, Menlo Park, Calif., at the price of $5.00 each postpaid. Some 36 speakers participated in the three major categories of discussion: methods of reaching high temperatures; materials suitable for high temperature use; and processes occurring at high temperatures. The three-day meeting, which was jointly sponsored by the Stanford Research Institute and the University of California, was attended by delegates from throughout the U. S. and abroad, and was distinguished for its broad treatment of the more difficult phases of high temperature research.

The Economics of Soviet Steel, by M. Gardner Clark, *Harvard University Press*, Cambridge 38, Mass., 400 pp., $7.50, 1956.—This four-part study, based almost entirely on Soviet sources, treats the development of the Russian iron and steel industry from 1917 to the present. The sections cover growth of production and investment, specialization and size of plants and equipment, factors affecting plant location, and productivity. Appendices and a bibliography are included. •

Chemical Production Flow Sheets, Plant Diagrams, *Deutsche Gesellschaft für chemisches Apparatewesen*, Frankfurt am Main 7, Germany, 40 sheets, approx. $4.00, 1957.—This set of diagrams, representing an enlarged edition of the out-of-print set entitled *Construction Flow Sheets, Symbols used for Equipment*, demonstrates the types of equipment which are most commonly used in chemical technology. It is particularly useful for descriptions of chemical processes in the literature, patent specifications, lectures, and for educational purposes, and facilitates an exchange of views between chemists and engineers.

A Study of Permanent Magnets of the Barium Ferrite Type, by K. J. Sixtus, *Office of Technical Services*, U. S. Dept. of Commerce, Washington 25, D. C., 53 pp., $1.50, 1957.—This report, sponsored by the Air Force, contains research on improvement of the magnetic properties of barium ferrite for use in ceramic permanent magnets. Data are provided on making the magnets, methods and results of physical measurements, and observations on theoretical aspects of magnetism in barium ferrite.

Corrosion Preventive Additives, two reports prepared by E. J. Schwoegler and L. U. Berman, *Office of Technical Services, U. S. Dept. of Commerce*, Washington 25, D. C., Part 2, 168 pp., $4.25; Part 3, 65 pp., $1.75; 1954.—These reports comprise two parts of a continuing Air Force project to develop and evaluate new corrosion inhibitors to replace or supplement petroleum sulfonates. They discuss tests on corrosion inhibition in mild steel, ball bearings in brass containers, SAE 1020 steel, and 52100 steel—Muntz metal brass.

Proceedings of the Porcelain Enamel Institute's 18th Annual Shop Practice Forum, *Porcelain Enamel Institute*, 1145 Nineteenth St., N. W., Washington 6, D. C., 137 pp., $5.00, 1957.—The proceedings of the three-day forum, held at the University of Illinois in November 1956, contain discussions on low temperature porcelain enameling, industry test methods, porcelain enamel on aluminum, metal preparation and milling, and enamel application and firing. •

MEMORANDUM:

From the Desk of the President

To: Purchasing Department

* * *

Investigate Davison's entry into the thorium and rare earths field. Understand they are producing materials which should be of interest to us. They have a reputation for dependability of products and service.

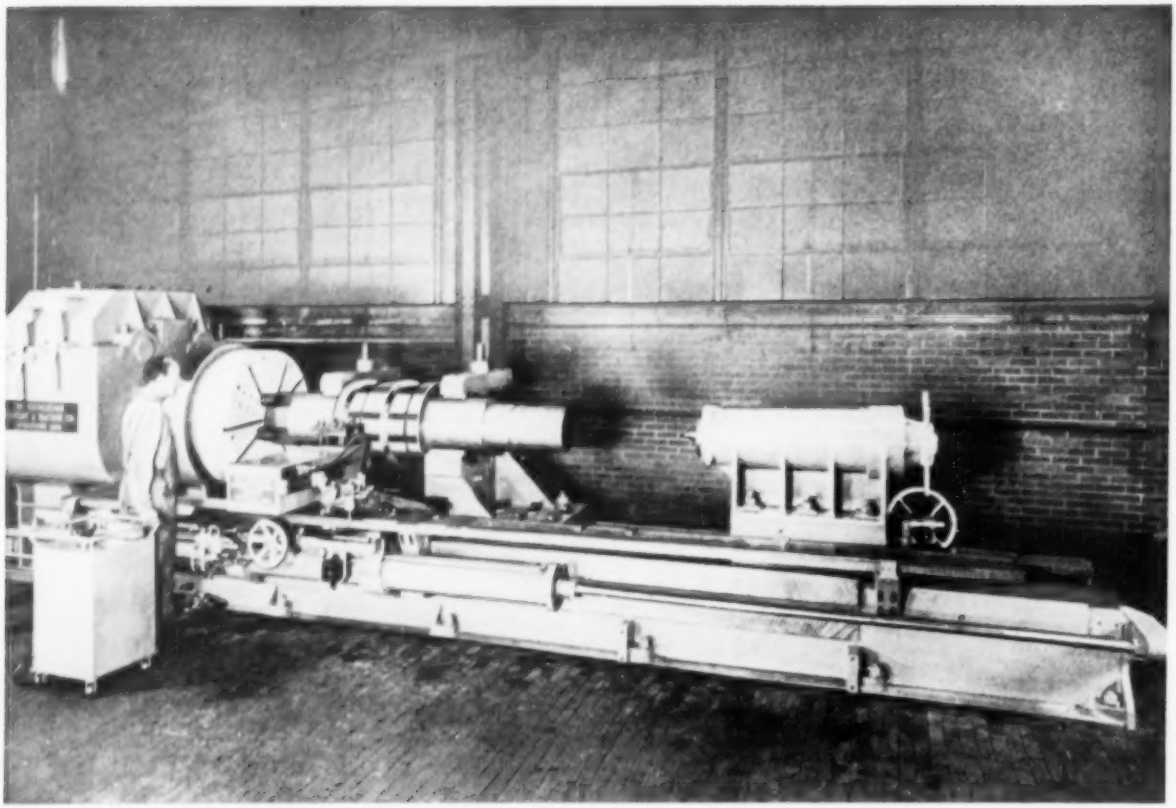
Two plants, one at Pompton Plains, N. J. (formerly Rare Earths, Inc.) and one at Baltimore, Md. are in operation. Your inquiries concerning products, samples and research and development services are welcome.

Progress Through Chemistry

DAVISON CHEMICAL COMPANY

Division of W. R. Grace & Co.

Baltimore 3, Md. and Pompton Plains, N. J.



New 36" contour roll lathe can turn parts on necks or centers . . . cut with single point carbide tools or with regular roll turning tools. Speeds range from .75 to 53.4 RPM. All heavy cast sections are ductile iron. Built by Youngstown Foundry and Machine Co., Youngstown, Ohio.

Ductile iron specified for heavy castings in new roll turning lathe

Today's machinist demands precision plus ruggedness in a roll turning lathe.

To meet these demands in its new 36" contour model, Youngstown Foundry and Machine turned to ductile cast iron for the lathe's four major castings.

For the face plate . . . ductile iron provided strength, toughness and wear resistance . . .

For the head stock . . . high strength along with good damping capacity . . .

For the tail stock . . . strength and toughness . . . a high modulus of elasticity . . .

For the carriage . . . high rigidity and strength.

Ductile cast iron provided these higher properties plus superior castability and machinability. That's because ductile iron combines certain advantages of steel and gray iron.

What about ductile cast iron for your application?

You may find ductile iron's combination of higher strength levels and good casting and machining characteristics will answer your design needs.

Why not find out how ductile cast iron can improve your product . . . save you production time and money.

Send for your copy of "Ductile Iron: The Cast Iron That Can Be Bent." It's packed with useful data.

ductile iron . . . the cast iron that can be twisted and bent

The INTERNATIONAL NICKEL COMPANY, Inc.
67 Wall Street, New York 5, N. Y.

Expansion for Lithium—the Lightest Metal

Dominion Magnesium Ltd., of Canada, has entered into the production of lithium at its Haley plant. Research for the U. S. Navy has shown that a Mg-12 pct Li alloy has the highest strength-weight ratio of any structural material, and has an exceptional capacity for deformation. Earlier this year, the three major U. S. lithium producers, American Potash & Chemical Corp., Foote Mineral Co., and Lithium Corp. of America, announced the formation of the American Lithium Institute, which will direct research on an industry-wide basis and act as an agency for distribution of technical information. For a survey of the past, present, and future of lithium, see p. 766.

Zinc Industry Apprehensive, Awaits Government Action

Closing down of the Eagle-Picher zinc mining and milling facilities in the Tri-State area and "suspension" of the Commodity Credit Corp. barter program have brought the problems of the zinc industry into sharp focus in recent weeks. The stockpiling program, which has been consuming about 15 pct of the total domestic zinc production, and the barter program, which reportedly imports more than the entire domestic consumption, have led to total zinc output which far exceeds the existing demand. The Government action was immediately reflected by a 2¢ drop in the East St. Louis price.

Statements by Gordon Gray, ODM Chief, have been indefinite. He stated that he expected government purchases for the stockpile to continue, at least for a while. This neither confirms or denies the earlier statement by an Assistant Secretary of the Interior, that stockpiling of the metal would cease "in a matter of months."

The barter program, whereby surplus farm commodities are traded abroad for foreign metals, is apparently in for thorough going-over, as both its political and economic effects have been under fire. St. Joseph Lead Co. has announced that it stands ready to stockpile its own production if Federal programs are not resumed.

Meanwhile, Congressmen from the mining areas are calling for governmental action for relief of both the lead and zinc industries. Other voices were heard in Congress—largely from budget-minded Congressmen—demanding that the ODM be abandoned and its duties be taken over by the Defense Dept., on a much reduced scale.

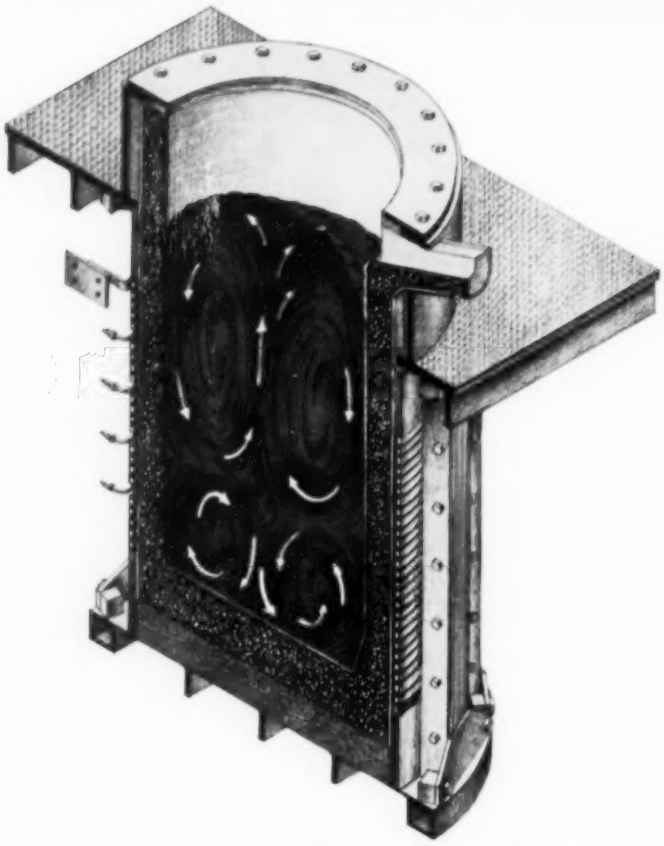
The market remains quiet, as both producer and consumer await further Government action.

Vacuum Technology: Key to Reactive Metal Production

Production of high-purity vacuum melted metals will receive a big boost when Vacuum Metals Corp., a division of Crucible Steel, completes a $1.5 million expansion program. Three-thousand pound ingots will be produced in a new vacuum induction furnace, expected to be the nation's largest. Already in operation, the new vacuum technology building of Electro Metallurgical Co. in Niagara Falls, N. Y., houses a variety of special experimental and pilot-scale furnaces, vacuum processing equipment, gas supplies, controls, and auxiliary instrumentation. Latest technical developments in this field, from the Los Angeles AIME Reactive Metals Conference, will appear in the July issue of JOURNAL OF METALS.

AJAX-JUNKER

a new principle in 60 Cycle induction melting



WHAT IT IS:

- A cylindrical induction coil supplied with ordinary 60 cycle current induces heat and vigorous electromagnetic stirring in the molten metal charge.

  Integrated electric controls regulate power, maintain high power factor automatically.

  Monolithic refractory linings are made by ramming against the sturdy water-cooled coil held in a rigid frame of magnetic and structural steel.

  This new principle was perfected in Europe over the last seven years. Over 100 Junker furnaces are now in use. AJAX-JUNKER designs are based on latest experience, using American components and practices throughout.

WHAT IT CAN DO:

- Outstanding results are proven in these fields:
  DUCTILE and ALLOY IRON CASTINGS
  RECOVERY OF IRON TURNINGS
  RECOVERY OF ALUMINUM SCRAP

  Available sizes range from 1 to 10 tons, with normal melting cycles from 2 to 4 hours. Power ratings are 200 kw through 1500 kw.

May We Explore the Possibilities of this New Method with You?

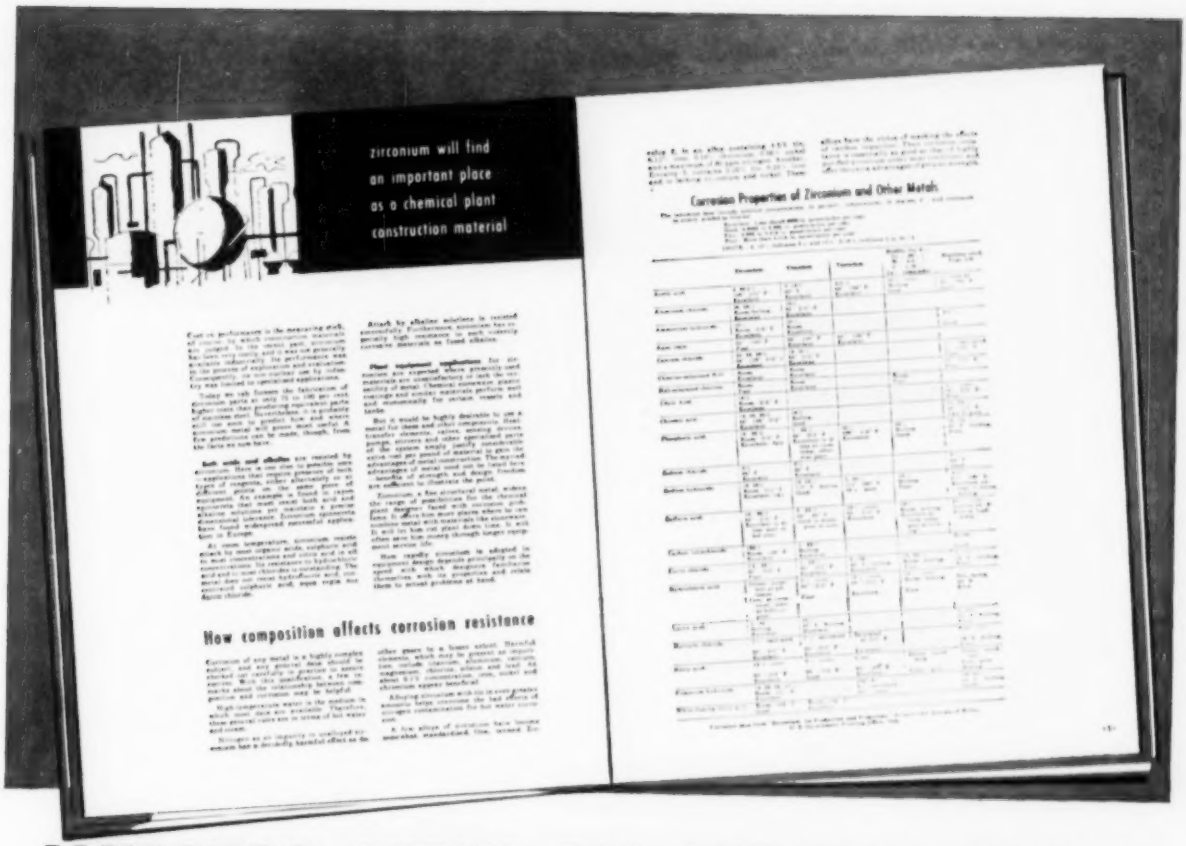
AJAX USA

60 CYCLE INDUCTION MELTING

ENGINEERING CORPORATION

TRENTON 7, NEW JERSEY

Associated Companies: Ajax Electrothermic Corporation Ajax Electric Company


zirconium will find
an important place
as a chemical plant
construction material
How composition affects corrosion resistance
Corrosion Properties of Zirconium and Other Metals

WHAT'S NEW ON ZIRCONIUM?

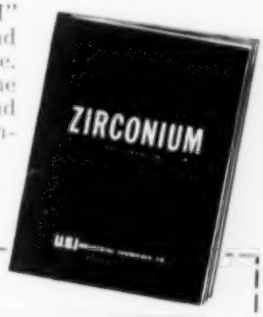
This U.S.I. booklet gives you information you can use . . . Send for a copy!

Today, with zirconium production trending sharply upward, and price downward, interest in this new and unique metal is growing rapidly.

To answer your questions about zirconium and its relative, hafnium, U.S.I. has prepared an informative new booklet — "ZIRCONIUM and HAFNIUM." The booklet gives the important facts on these newly available metals . . . lists important mechanical and physical properties of both . . . describes briefly the new semi-continuous sodium reduction process for production of zirconium and hafnium.

You'll find the outstanding corrosion properties of zirconium compared with other important metals... phase diagrams of twenty binary alloy systems . . . descriptions of several fabrication techniques.

You're sure to find "ZIRCONIUM and HAFNIUM" valuable in discussions and as a preliminary reference. For your copy, forward the coupon today . . . or just send your name on your company's letterhead.



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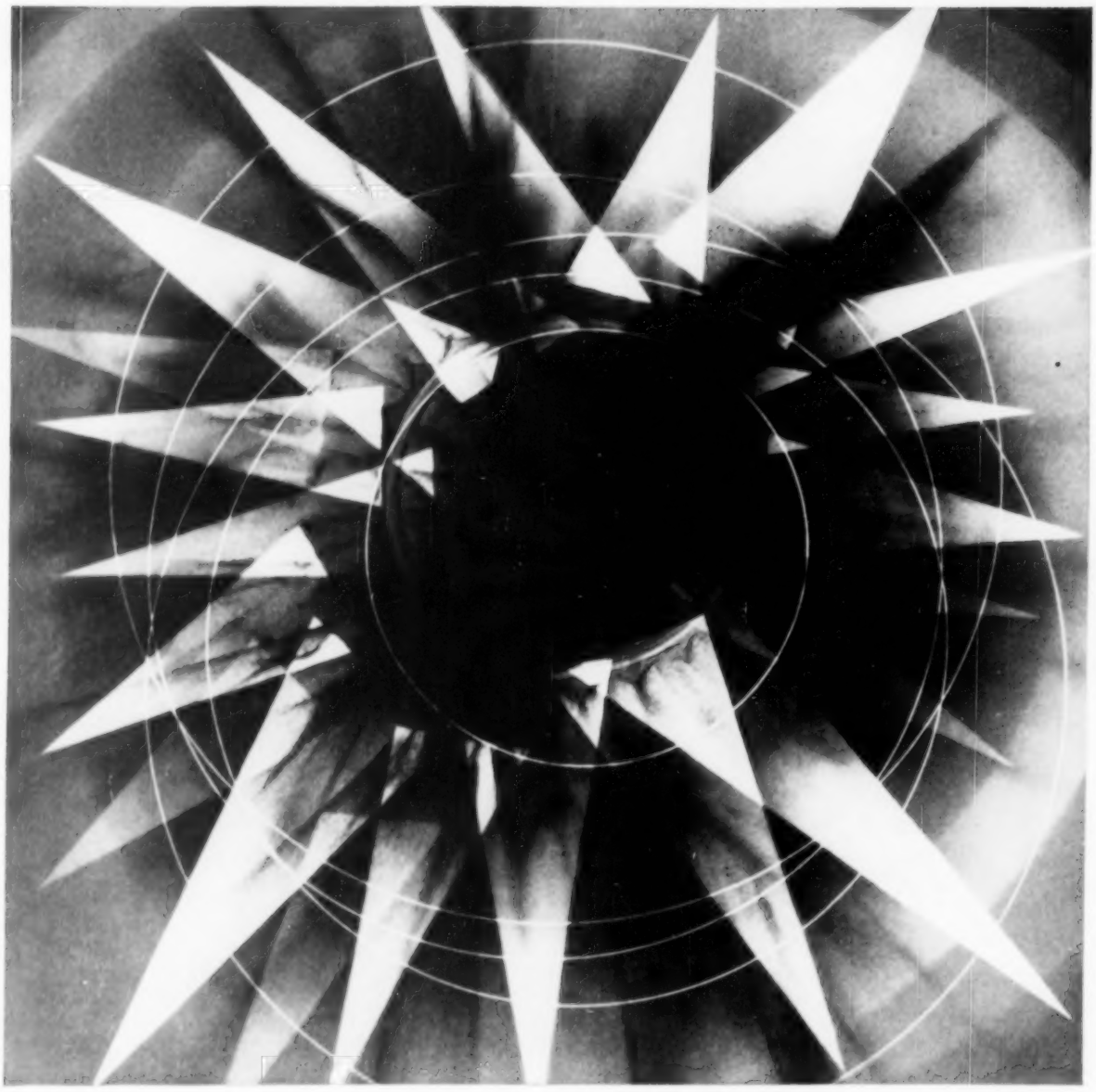


breaking the barriers
with Utica Vacuum Metals

Now that supersonic flight has become routine, today's challenge lies in developing *metals* and *means* of cracking the thermal barrier.

The metals problem has already been partially solved by superalloys produced through Vacuum Melting. This process, as developed by Utica, has yielded such super refractory alloys as Udimet 500 — a clean, pure alloy combining unsurpassed stress-rupture life with superior high tensile strength in the 1200° F to 1800° F range. *At 1600° F, Udimet 500 has a tensile strength of over 100,000 PSI.*

In addition to the development of new and superalloys, Utica specializes in upgrading the quality of existing alloys.

VACUUM MELTING
provides these properties

- High temperature corrosion resistance
- Increased ductility
- Extreme cleanliness
- Precise chemical control
- Longer stress-rupture life
- Increased tensile strength
- Better fatigue resistance
- Greater yield strength
- Greater impact resistance
- Greater creep properties

UTICA METALS DIVISION OF KELSEY-HAYES

UTICA DROP FORGE & TOOL DIVISION — KELSEY-HAYES CO., UTICA 4, NEW YORK

EDITORIAL

Aims and Objectives—

The Metallurgical Society of AIME

THE basic reason for creating a Metallurgical Society within the framework of the American Institute of Mining, Metallurgical, and Petroleum Engineers was to provide a complete organization for metallurgists, covering the handling of metal from ore out of the ground to the finished article delivered to the customer.

Also, the Metallurgical Society can be of great assistance in the professional development of all metallurgists. This advancement or development in professional ability will crystallize when all members of the Society utilize the Society for pooling their individual talents towards the discovery of greater use for metals and improvement in quality of existing metals. This could be of measurable assistance in alleviating current problems in various segments of our mining industry served by our sister society, the Society of Mining Engineers of AIME. The result will be expansion of markets, thus a healthier mining industry and further improvement in our standard of living.

The aims and objectives of the Metallurgical Society as specified in the Bylaws are to promote the advancement of metallurgical knowledge and the advancement of the metallurgical profession as a whole by providing a medium for communication and cooperation among those interested in any phase of theoretical and applied metallurgy; to provide an organization to represent the metallurgists and metallurgical engineers on matters pertaining to education; to disseminate metallurgical knowledge by the holding of professional meetings; and to provide high standards in the profession of metallurgical engineering.

It is felt that these aims and objectives can well be accomplished by the Society which is formed of the three divisions of the old Metals Branch. These divisions are the Institute of Metals Division, Iron and Steel Division, and the Extractive Metallurgy Division.

In order to allow a comprehensive study of all aspects of the metallurgical profession, both functional and commodity committees have been set up under each of the divisions. Under the Institute of Metals Division, such functional committees exist as High-Temperature Alloys, Metal Science, Nuclear Metallurgy, and Powder Metallurgy. Under the Iron and Steel Division, the functional committees include Blast Furnace, Coke Oven, and Raw Materials; Converter Steel; Electric Furnace Steel; Mechanical Working; Open Hearth Steel; and Physical Chemistry of Steelmaking. Functional and commodity committees under the Extractive Metallurgy Division are: Electrolytic Extractive Processes; Hydrometallurgy; Physical Chemistry of Extractive Metallurgy; Pyrometallurgy; Reduction and Refining of Copper and Nickel; Lead and Zinc; Aluminum and Magnesium; Refractories; and Titanium, Uranium, and Uncommon Metals.

In organizing the Metallurgical Society, an endeavor was made to provide standing committees, reporting directly to the Officers and Directors, that could fulfill the objectives of the Society, and not conflict with areas that are better handled within a Division. Such Society committees are the Committee on the Metallurgical Profession, Education Committee, the Finance Committee, and the Admissions Committee. Other standing committees, such as the Programs Committee and the Publications Committee, will work in conjunction with their Division counterparts.

As specified in the Bylaws, the new Society will endeavor to provide for the oral presentation and printed distribution of technical papers. The range of papers will include the results of fundamental research, the application of the research results, review or symposium-type papers, and papers on education and professionalism. These should be of inestimable value not only to the members of the Metallurgical Society but also to members of the other Societies of AIME.

In the original planning for the Metallurgical Society, it was felt that the Bylaws should provide a framework for an active organization that would not only meet the needs of all metallurgists, but would also provide for growth and diversification as the Society progressed. As an example of pending change, we now have a committee studying our overall publications policy. It may be that, as the organization grows, we will find need to expand the number of committees or add additional divisions to the Society.

In any event, we have established a foundation that will, we are sure, accomplish its fundamental aim—to provide a complete organization for metallurgists covering the handling of metal from ore out of the ground to the finished article delivered to the customer.

J. C. Kinnear, Jr.

President, Metallurgical Society of AIME

Bell Laboratories researchers Henry S. McDonald, Dr. Eng. from Johns Hopkins, and Max V. Mathews, Sc.D. from M.I.T., examine magnetic tape used in new research technique. Voice waves are converted into sequences of numbers by periodic sampling of amplitudes, 8000 samples per second. General purpose electronic computers act on these numbers as a proposed transmitting device might.

They send real voices on imaginary journeys

In their quest for better telephone service, Bell Laboratories researchers must explore many new devices proposed for the transmission of speech signals. For example, apparatus can be made to transmit speech in the form of pulses. But researchers must always answer the crucial question: how would a voice sent through a proposed device sound to the listener?

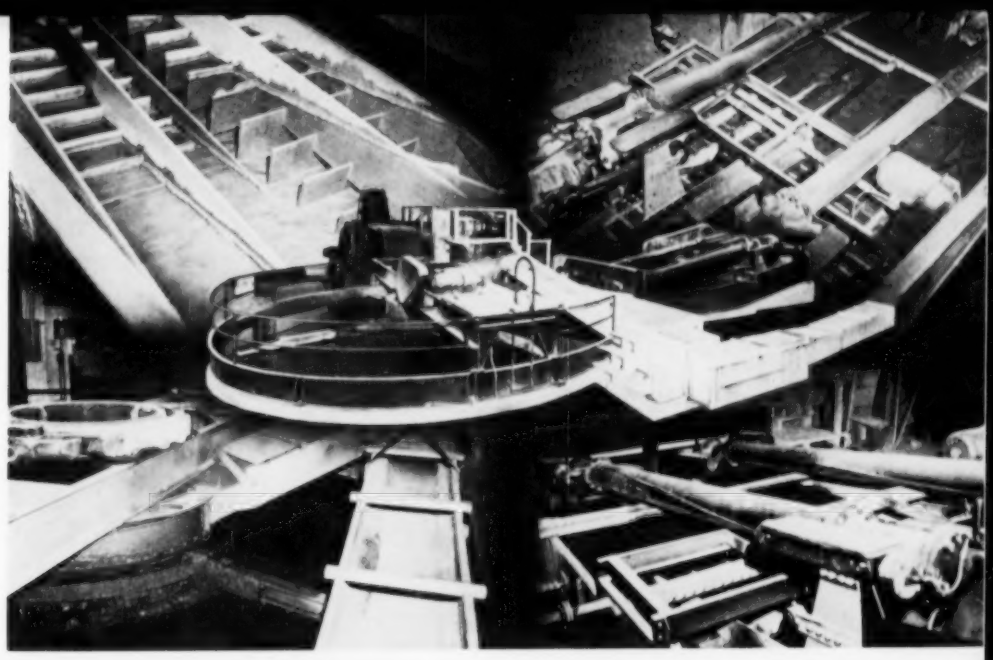
In the past it often has been necessary to construct costly apparatus to find out. Now the researchers have devised a way to make a high-speed electronic computer perfectly imitate the behavior of the device, no matter how complicated it may be. The answer is obtained without building any apparatus at all.

The researchers set up a "program" to be followed by the computer. Actual voice waves are converted into a sequence of numbers by sampling the waves 8000 times per second. Numbers and program are then fed into the computer which performs the calculations and "writes out" a new sequence of numbers. This new sequence is converted back into real speech. Listeners hear exactly how well the non-existent device could transmit a real voice.

With this novel technique, new transmission ideas are screened in only a fraction of the time formerly required. Thus valuable time and scientific manpower are saved in Bell Laboratories' constant search to provide still better service for telephone customers.

BELL TELEPHONE LABORATORIES

World center of communications research and development



HYDROMETALLURGY 1957

THE 1957 Annual Meeting provided the time and place for the Hydrometallurgy Committee's annual sessions. New developments in the field and the strong physical-chemical tenor of the meetings justifies a brief review of the current status of this field of extractive metallurgy.

Hydrometallurgical processes over the years have been largely liquid-solid reactions involving selective dissolution and selective precipitation of specified metallic elements. Some of the most critical problems encountered have been the unit operations variety, for example:

a) Comminution
b) Agitation
c) Liquid-solid separation
d) Clarification.

During the current mid-century, the advent of new and superior materials of construction has encouraged an adventure into more rigorous treatment processes. High temperature and/or high pressure techniques applied to dissolution chemistry have led to an unrivaled competition between the concept of a near universal solvent for raw materials versus a near insoluble material for containers. In these systems the role of hydrogen and oxygen has been expanded for precipitation as well as solubilization.

The investigation and application of new processes has also helped in solving of unit operation problems. The separation of liquids and solids involving thickening, filtering, and clarification can be minimized by use of ion exchange techniques employing solid resins or immiscible liquid phases. In these processes an aqueous pulp often can have the selected metallic ion extracted without a complete liquid-solid separation.

New processes like new ideas are not a panacea, nor are they always economically desirable. The separation of rare earth metals, of hafnium from zirconium, and the recovery of uranium can tolerate more exotic treatment than the more mundane metals.

In order to apply, develop, and control processes in this new age, it became necessary to develop a theoretical tool to guide the operator before he either erected a new processing plant or rejected the more prosaic processes. At this stage, some of the physical chemists have become the design engineers of a new hydrometallurgy. A re-examination of the thermodynamics and kinetics of the metallurgical processes has opened the way for innovation and economy, the watchwords of modern engineering.

Pressure systems at elevated temperatures have made it possible more completely to bridge the gap between aqueous metallurgy and fusion metallurgy. It permits thermodynamic and kinetic advantage to be obtained in aqueous systems which are kinetically unfavorable at ambient temperatures. It has lifted the boiling point of water to a point where we have, in effect, a new medium. It has increased the solubility of gaseous species to an extent that they enter into reactions with a vigor unmatched in previous aqueous systems. We have arrived at a stage where kinetics is a necessity to design, not a theoretical after-thought.

In the papers to follow, an attempt has been made to blend application and theory for the purpose of stimulating thought among operators and theorists alike.—*H. Gordon Poole, Chairman, Hydrometallurgy Committee*

HYDROMETALLURGY

Atmospheric vs Pressure Leaching of Uranium Ores

Pilot plant studies reveal that high temperature, high pressure leaching of uranium ores in alkaline solutions cuts leach time 90 to 95 pct. Leach times may be cut in half by using existing Pachuca tank equipment at moderate temperatures and pressures.

By R. G. Beverly, A. W. Griffith, and W. A. Millsap

THE Grand Junction Pilot Plant, operated by National Lead Co. Inc., for the U. S. Atomic Energy Commission, is engaged in the amenability testing of ore bodies to establish design and cost data for commercial mills and to test new processes for recovery of uranium from ores. Test work was performed to study the effects of several variables on leaching of uranium ores in carbonate solutions. Many of these variables had been investigated in the laboratory, but pilot plant tests were desirable to evaluate their importance in semi-works equipment and to predict optimum operating conditions for future commercial mills. The results of these tests should serve as a guide in selecting the most efficient and economical method of leaching uranium ores amenable to a carbonate process.

This paper is concerned with a process in which uranium is extracted from the ore by a hot Na_2CO_3-$NaHCO_3$ solution; the uranium bearing solution is separated from the solid residue by filtration, and uranium is then precipitated by chemical means.

Chemistry of Alkaline Leaching

The important reactions involved are shown below. The literature contains a number of detailed reports on the chemistry of alkaline leaching.[1-3]

$$2UO_2 + O_2 \rightarrow 2UO_3 \quad [1]$$

$$UO_3 + H_2O + 3\,Na_2CO_3 \rightarrow Na_4UO_2(CO_3)_3 + 2\,NaOH \quad [2]$$

$$Na_4UO_2(CO_3)_3 + 4\,NaOH \rightarrow Na_2UO_4 + 3\,Na_2CO_3 + 2\,H_2O \quad [3]$$

$$NaOH + NaHCO_3 \rightarrow Na_2CO_3 + H_2O \quad [4]$$

$$UO_3 + Na_2CO_3 + 2\,NaHCO_3 \rightarrow Na_4UO_2(CO_3)_3 + H_2O \quad [4a]$$

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4 \quad [5]$$

$$4\,FeS_2 + 15\,O_2 + 16\,Na_2CO_3 + 14\,H_2O \rightarrow 4\,Fe(OH)_3 + 8\,Na_2SO_4 + 16\,NaHCO_3 \quad [6]$$

$$SiO_2 + 2\,Na_2CO_3 + H_2O \rightarrow Na_2SiO_3 + 2\,NaHCO_3 \quad [7]$$

The first reaction shows the oxidation of uranium from quadrivalent to hexavalent. Reaction 2 represents the dissolution of uranium by the carbonate. In the absence of bicarbonate, uranium will precipitate as a sodium uranate, reaction 3, as the hydroxide increases. Therefore, sodium bicarbonate is added, reaction 4, and the dissolution of uranium in the carbonate and bicarbonate solutions can be represented by 4a the summation of equations 2 and 4. Reaction 5 is a carbonate consumer which usually eliminates the advantages of using alkaline leaching for ores containing appreciable amounts of gypsum. Although reactions 6 and 7 also consume Na_2CO_3, part of the sodium ion results in $NaHCO_3$, which is useful to the process. The sodium sulfate is of no use and, as far as is known, has no effect on leaching. Sulfate concentrations up to 50 g per liter have been experienced in the pilot plant with no detrimental effect and laboratory leach tests made with sulfate concentrations as high as 100 g per liter showed no decrease in uranium extraction.

R. G. BEVERLY and W. A. MILLSAP are Acid Plant Superintendent and Metallurgical Engineer, respectively, National Lead Co. Grand Junction Pilot Plant. A. W. GRIFFITH, formerly Acid Plant Superintendent, National Lead Co. Grand Junction Pilot Plant, is now associated with Federal Uranium Corp. Paper presented at AIME Annual Meeting, New Orleans, February 1957.

The silica reaction (Eq. 7), which is favored by temperatures above 250°F, may decrease filtration rates, and the silicate upon cooling may precipitate and occlude some uranium. However, in pilot plant autoclave leaching operations, this has not happened, even at temperatures of 275°F. Filtration rates on residues from high temperature leaching have been somewhat lower than those from leach tests at 180°F. Although the exact reason for the lower filterability has not been established, the formation of silicates probably is contributory.

Alkaline Leach—Filtration Pilot Plant

The flowsheet of the Alkaline Leach—Filtration Pilot Plant is shown in Fig. 1 and has been described in detail in other reports.[1,2]

The ore, after being crushed to −3/16-in., is fed to a 3 x 5-ft ball mill operating in closed circuit with an 18-in. rake classifier. Recycled mill solution is used for grinding solution. The classifier overflow is pumped to a 12 x 8-ft thickener to thicken the pulp and to maintain a constant pulp density to the leach circuit.

Pachuca Tanks: The leach circuit consists of either four 4 x 47-ft Pachuca tanks in series or a 4.5 x 12-ft autoclave. The four Pachucas provide a leach contact time of 96 hr with a 50 pct solids slurry at a feed rate of 12 tons of ore per day. Each Pachuca has a 3-in. internal air lift for pulp circulation, two ¼-in. pipes in the cone for adding aeration air, and four 1-in. steam pipes to maintain desired pulp temperatures. The vessels are insulated with 1-in. Fiberglas and a corrugated aluminum covering. The 45-ft elevation to the discharge level provides a pressure of approximately 30 psig in the bottom of the tank when filled with a 50 pct solids pulp. Although the Pachucas are usually operated at atmospheric pressure on top, the installation of a pressure regulating valve on the top of each tank has permitted operating under pressure up to 20 psig on top, which results in a pressure of 50 psig at the bottom. The Pachucas are shown in Fig. 2.

Autoclave: When the autoclave is in operation, it replaces the Pachucas in the circuit. Pulp is heated by steam in a double pipe heat exchanger. Retention time in the autoclave is approximately 6.5 hr at 50 pct solids. The pulp is maintained at the desired leaching temperature by automatically controlled electrical strip heaters fastened to the bottom of the autoclave between the shell and the insulation. However, only a small amount of heat is required for this purpose. The autoclave is shown in Fig. 3.

The horizontal autoclave is 4½ ft. in diameter, 12 ft long, with 1½-ft dished heads, and is divided into three sections by double baffle plates. Each section is agitated with a 5 hp turbine-type agitator equipped with a 5-blade 16-in. turbine. Capacity of the vessel is approximately 1200 gallons. Air is added through a ½-in. line discharging beneath each agitator. The quantity of air input is regulated by an automatic control valve. A spring-loaded reducing valve controls the pressure in the autoclave. Pulp is discharged by the internal pressure through an intermittently operated plug valve. The discharge valve is operated automatically by a pulp level control and is open approximately 1 min at 20-min intervals. Temperature and pressure losses in the discharge line between the autoclave and the top of a Pachuca which is used as a surge vessel dissipate enough heat and pressure so that very little flashing of steam takes place at the discharge. As yet, no attempt has been made to utilize the heat in the discharging pulp for preheating the incoming pulp. It is interesting to note that the Canadians at the Beaverlodge mill estimate a savings in heating costs of $0.20 per ton by this method of heat recovery from autoclave leach pulp.[3]

The leached pulp is discharged from the Pachucas or autoclave to the first of three 4 x 8-ft cloth-covered vacuum drum filters operating in series. Provisions are made to add filtering aids to the pulp feed for each filter. The filtrate from the first filter is pregnant liquor containing the solubilized uranium. This liquor is pumped through a plate and frame clarification press and then to the precipitation tank. The solids residue is washed on the second and third filters and is pumped to tailings. The repulp solution and wash to the second filter is barren filtrate from the regeneration tank. The solids fed to the third filter are repulped and washed with water. Filtrate from the second filter is returned to the grinding circuit, and filtrate from the third filter is used as wash on the first filter.

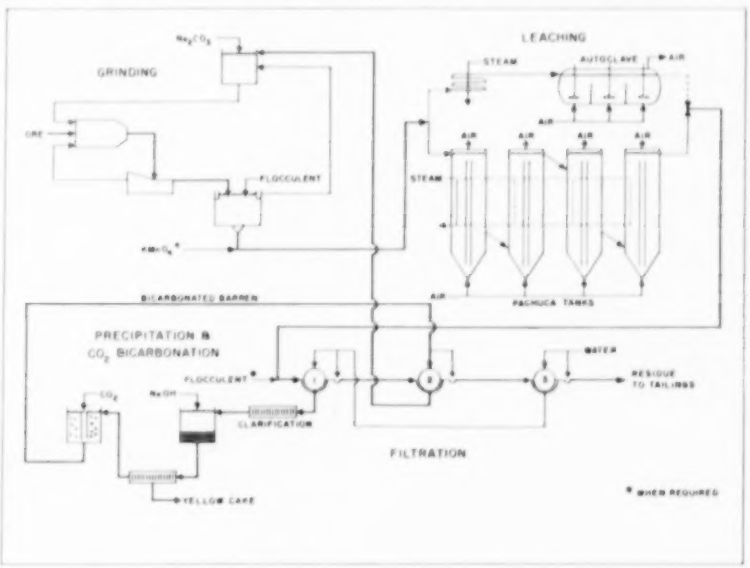
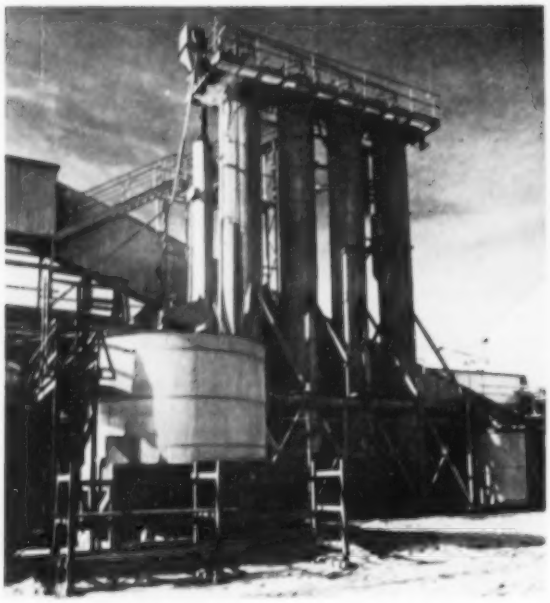


Fig. 1—Flow sheet of the alkaline leach filtration process used at the Grand Junction Pilot Plant. Either Pachuca tanks or the autoclave may be used, all other factors remaining constant.



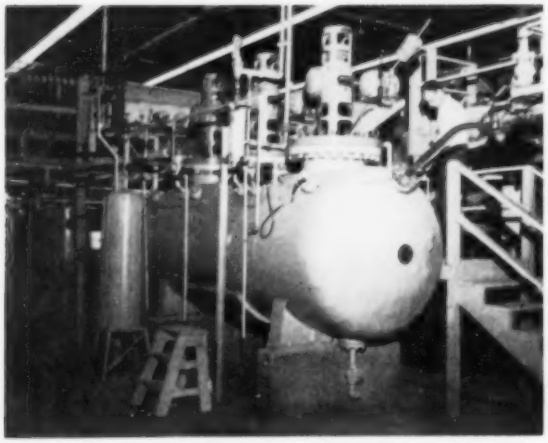


Fig. 2—(left) Pachuca leach tanks used in the pilot plant. It is 45 ft from the bottom of the tank to the pulp overflow line, and a ½ in. line provides air for the 3 in. air lift. Inside diameter is 4 ft.

Fig. 3—(above) Pilot plant 1200 gal autoclave. Measuring over 12 ft long, the unit is provided with three 5 hp 230 rpm mechanical agitators. Inside diameter is 4½ ft and it is filled to a level of 3½ ft.

Factors Affecting Leach

At atmospheric pressure, relatively long contact times are required for alkaline leaching—50 to 100 hr. For good uranium extraction, a hot leach is required, and temperatures above 180°F, up to 250° or 275°F, decrease the contact time required to 6 or 10 hr. Oxidation of the reduced uranium in the ore can be accomplished chemically, usually by $KMnO_4$, or by air. Higher pressures increase the solubility of oxygen in the leaching solution and permit the use of less air for oxidation. Reagent concentrations are usually maintained in the range of 40 to 60 g Na_2CO_3, and 10 to 20 g $NaHCO_3$ per liter. Agitation should be adequate to keep the pulp in a constant and thoroughly fluid regime. The dispersion of oxidation air throughout the pulp is also dependent on the mixing device. Most ores require grinding to grain size in order to permit contact of the uranium particles with the leach solution. Grinds usually average 1 to 5 pct +65 mesh and 50 to 75 pct −200 mesh. Pulp densities are usually controlled between 40 and 55 pct solids, a range which permits adequate mixing and prevents rapid settling of the coarser sands.

The following factors are of importance in alkaline leaching.[2, 8, 10]

Leach Contact Time: The required contact or retention time of the ore in the leach solution is dependent upon temperature, efficiency of oxidation and agitation, and to an extent on the other variables. Fig. 4 shows the results of alkaline leach studies conducted on La Sal ore, from the Big Indian Wash area of Utah.[2] Of the total leach extraction, a large part takes place in the first few hours, providing sufficient oxidation and agitation are present, but a much longer time is required to raise the extraction to a leveling-off point. Pilot plant results at higher pressures have shown even a more pronounced effect with 95 pct of the total leaching taking place within the first 1 or, at most, 2 hr.

Leach Temperature: Fig. 5 shows the comparison of autoclave and Pachuca leaching and the relationship between increased temperatures and pressures on extraction and contact time. These studies were made while processing Todilto Black Limestone from Grants, New Mexico,[3] and Rio de Oro ore from Ambrosia Lake, New Mexico.[7] Todilto Limestone

Table I. Autoclave Leach Studies on La Sal Ore*

Test No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ore head assay, pct U_3O_8	0.350	0.307	0.294	0.354	0.328	0.323	0.332	0.309	0.346	0.358	0.349	0.352	0.402	0.437	0.376
Leach Conditions†															
Pressure, psig	30	33	30	50	53	54	51	55	53	53	70	70	70	70	70
Temperature, °F	225	250	250	225	251	250	250	274	271	273	225	250	250	250	267
Air, std cu ft per ton ore	952	665	1060	990	738	1110	1475	738	1110	1475	990	183	1100	2080	990
Extraction															
Final residue, pct U_3O_8	0.025	0.023	0.021	0.018	0.012	0.011	0.013	0.022	0.017	0.018	0.016	0.014	0.014	0.014	0.014
U_3O_8 extraction, pct															
after 2.4 hr	88.3	88.9	89.5	88.7	93.9	94.1	93.4	89.6	92.2	92.7	90.8	93.5	94.8	94.7	94.1
after 4.8 hr	91.1	91.2	91.8	92.9	95.3	96.0	95.5	91.6	94.2	94.4	94.6	95.2	96.0	96.1	95.7
after 7.2 hr	92.9	92.5	92.9	94.9	96.3	96.6	96.1	92.9	94.5	95.0	95.4	96.0	96.5	96.8	96.3
Terminal Reagent Concentration															
g Na_2CO_3 per liter	39.1	40.3	39.0	35.0	39.7	38.3	41.1	36.1	39.7	41.9	37.5	40.1	40.5	37.6	35.0
g $NaHCO_3$ per liter	10.5	12.6	12.0	13.5	13.2	13.3	13.1	16.7	15.2	13.8	14.0	20.8	19.3	17.9	16.3

* Pulp specifications:
Pulp Density: 50 pct solids
Average Grind: 1.1 pct +65 mesh, 71.5 pct −200 mesh
Reagent Concentration (Grinding Solution): 49 g Na_2CO_3 per liter, 8 g $NaHCO_3$ per liter
Ore Feed Rate: 11.8 tons per day

† Underline indicates major variable changed from previous test.

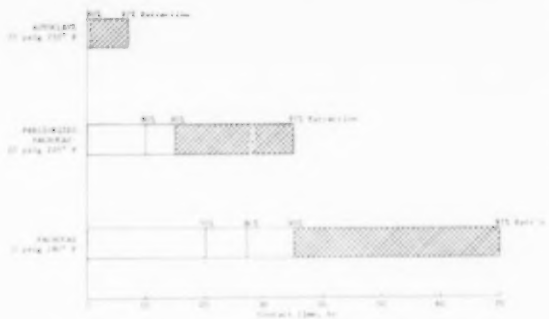


Fig. 4—Effect of temperature and pressure on contact time using La Sal ore.

contains approximately 81 pct $CaCO_3$ and Rio de Oro ore treated in the pilot plant assayed 7.5 pct $CaCO_3$. Leaching at atmospheric pressure and 180°F required 10 to 20 times the contact time necessary at elevated pressures and at temperatures in the range of 255 to 265°F.

Oxidation and leaching pressure: The pertinent data from a series of autoclave tests are shown in Table I, and the more important results are shown graphically in Fig. 6 and 7. Effectively no uranium in the reduced state will be extracted from the ore without oxidation. Oxidation can be accomplished by chemical means, usually $KMnO_4$ in alkaline solutions, or by air, as was done in all tests in the pilot plant. At a pressure of 30 psig, the partial pressure and solubility of oxygen is 3.4 times higher than at atmospheric pressure. This relationship continues, and at 100 psig the solubility is increased 9 times. Increasing the temperature has the reverse effect and the solubility of oxygen decreases. For any particular pressure and temperature condition, there is an optimum quantity of air addition above which no benefits in extraction will be realized.

During the autoclave studies the lowest extractions (92 to 93 pct) were obtained at a pressure of 30 psig even though the temperature was increased from 225° to 250° F and the air was also increased. When the pressure was raised to 50 psig and the temperature to 250°F, extraction increased to over 96 pct. Higher air rates at these conditions gave no appreciable improvement. Increasing the temperature to 270 to 275°F dropped extraction to 93 pct but higher air rates at these temperatures showed a significant improvement.

Comparing Tests 5 to 7 with 8 to 10 in Table I clearly shows the detrimental oxygen solubility effect from increasing temperatures without a corresponding increase in pressure; extraction at a pressure of 70 psig and a temperature of 250 to 270°F was no better than at 50 psig and 250°F. In the autoclave, a temperature of 250°F, a pressure of 50 psig, and air addition between 800 and 1000 std cfm per ton of ore results in highest extractions.

The Pachuca studies, shown in Table II and Fig. 8, were made primarily to determine the effect of varying quantities of aeration air at temperature levels of 180° and 220°F. Aeration air is usually held in the range of 20 std cfm per Pachuca (1.6 std cfm per sq ft cross sectional area). Between 3.0 and 5.0 std cfm is used in each Pachuca air lift. As can be noted in Table II and Fig. 8, reducing the air below 20 std cfm per Pachuca lowered extraction. However, 3320 std cfm of air per ton with a 32 hr leach at 20 psig and 220°F was as effective as 5000 std cfm per ton with a 48-hr leach at atmospheric pressure and 180°F.

In general, uranium recovery decreased as the aeration air rate was decreased. It is evident from these data that extraction rates increased with higher temperature and pressure. As in the autoclave, oxygen solubility increases with pressure, and dissolution rate increases with temperature. However, temperatures were not high enough to show oxygen solubility impairment.

Sodium Carbonate and Bicarbonate Concentration: Reagent concentrations in alkaline leach solutions are usually controlled in the range of 40 to 60 g Na_2CO_3 and 10 to 20 g $NaHCO_3$ per liter. They may be varied over a wider range, particularly much higher in carbonate strength, but pilot plant studies have shown no major effect on extraction between 25 and 60 g Na_2CO_3 per liter and 5 to 25 g $NaHCO_3$. At low concentrations filtration rates were appreciably reduced. The optimum amount of $NaHCO_3$ should be determined and the concentration held at that level because the higher the $NaHCO_3$ concentration in the pregnant liquor, the more caustic soda will be required for precipitation.

It has been noted that with carbonate consuming ores, more carbonate is consumed in pressure leaching than at atmospheric pressure. On some ores the bicarbonate strength in the grinding solution has been as low as 5 g per liter, yet the solution will leave the leaching step at 15 g per liter or higher. Other ores will result in a complete reversal of this chemistry and produce some carbonate at the expense of the bicarbonate. The amount of uranium in the leaching solution did not have an effect on extraction in the pilot plant.

Reagent consumption can be broken down as an average of 16 lb Na_2CO_3 and 18 lb NaOH per ton of ore. Fuel oil consumption for regeneration will vary between 0.4 and 0.6 gal No. 2 fuel oil per ton. Reagent consumption data from one amenability test in which the ore was treated in the autoclave and the Pachucas indicate from 5 to 8 lb more NaOH per ton of ore are needed in the autoclave than in the Pachuca tanks. This difference is presently under further investigation.

Agitation of Pulp: Pachuca leaching utilizes internal air lifts for agitation of the pulp. Air lifts

Table II. Pachuca Leach Studies on La Sal Ore*

Test No.	1	2	3	4	5
Ore head assay, pct U_3O_8	0.429	0.434	0.379	0.350	0.394
Leach Conditions†					
Top pressure, psig	0	0	20	20	20
Temperature, °F	183	182	217	222	222
Air,‡ std cu ft per ton ore	2500	5000	830	1660	3320
Number of Pachucas	3	3	2	2	2
Extraction					
Final residue, pct U_3O_8	0.018	0.009	0.023	0.011	0.009
U_3O_8 extraction, pct					
after 16 hr	77.9	88.7	82.3	87.4	92.9
after 32 hr	91.6	95.9	93.9	96.9	97.7
after 48 hr	95.8	97.9	—	—	—
Terminal Reagent Concentration					
g Na_2CO_3 per liter	48.6	49.9	48.7	45.0	44.6
g $NaHCO_3$ per liter	13.9	12.6	11.4	12.0	14.6

* Pulp specifications:
Pulp Density: 30 pct solids
Average Grind: 2.3 pct + 65 mesh, 68.1 pct − 200 mesh
Reagent Concentration
(Grinding Solution): 52 g Na_2CO_3 per liter, 9 g $NaHCO_3$
Ore Feed Rate: 17.4 tons per day

† Underline indicates major variable changed from previous test.

‡ In addition to air lift air which amounted to 4 std cfm per Pachuca.

are advantageous in that no moving parts are involved, but properly designed mechanical agitators assure far more complete mixing. Where mechanical agitators will tend to break down particle size somewhat, air lifts have little tendency to do so.

An agitator which efficiently mixes the pulp will tend to break the air bubbles, thus increasing the air to pulp surface contact area. The liquid film surrounding the air bubbles is reduced in thickness by thorough agitation which increases the mass transfer coefficient of oxygen through the film and into solution. Greater oxidation effect of the air is also accomplished if, through complete mixing, the air is retained in the pulp a longer time and bubbles of air do not rise immediately to the surface from their point of discharge into the pulp.

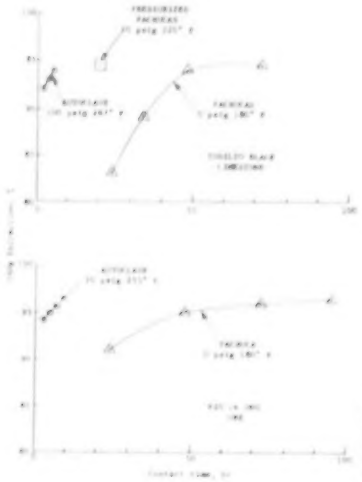


Fig. 5—Contact time vs. temperature and pressure for two ores.

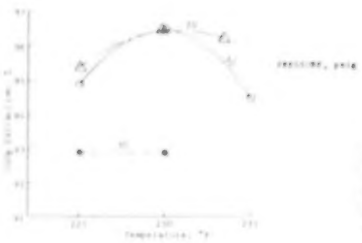


Fig. 6—Effect of temperature and pressure, autoclave studies on La Sal ore.

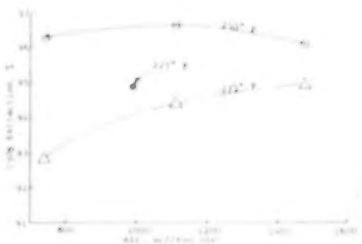


Fig. 7—Effect of air addition at 50 psig, autoclave studies on La Sal ore.

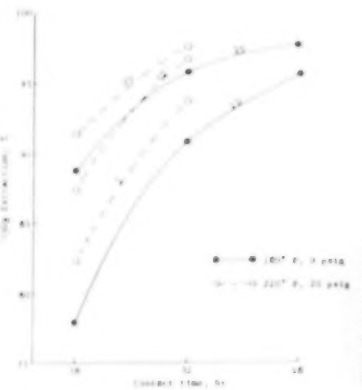


Fig. 8—Pachuca leach studies on La Sal ore. Numbers on plots refer to air addition, in std cu ft per min per Pachuca.

Some comparisons of leaching in Pachucas and in conventional mechanically agitated leach tanks indicate contact time is reduced appreciably by more thorough agitation, but more investigative work needs to be done.

Fineness of Grind: Carbonate liquors do not tend to dissolve interstitial material and it is necessary to grind to the grain size of the ore to permit contact of the uranium particles with carbonate solution. Pilot plant grinding, which reduces the ore to 2 pct +65-mesh and 70 pct −200-mesh material, has been adequate for high uranium extraction.

Pulp Density: Degree of agitation is related to pulp density. If pulp densities are too high to permit adequate mixing, extraction will suffer. When using air agitation, such as air lifts in the Pachucas, pulp densities greater than 50 pct solids can reduce extractions, other factors such as temperature and contact time being equal. An example of this is one test made in the Pachuca tanks on Rio de Oro ore. At 51 pct solids, extraction was 95.4 pct in 60 hr time and 96.5 in 100 hr. When leaching at 59 pct solids, extractions were 94.7 pct in 60 hr and 95.4 pct in 100 hr, showing approximately a 1 pct lower recovery or 0.05 lb U_3O_8 per ton.

Autoclave Corrosion

The Canadians at the Beaverlodge mill have experienced a pitting type of corrosion at the froth or splash line in the autoclave, and little or no corrosion has been observed elsewhere. The attack is attributed to the high sulfide content of the ore and takes place in the autoclaves near the head of the leach circuit. The reaction is thought to be from sulfurous or sulfuric acid which is formed from the sulfide as the plup, which splashes on the walls, is diluted by condensed water vapor. The solution near this froth area is changed from alkaline to acidic.

A clad belt of low carbon, type 316, stainless steel in the area of the pulp level could minimize this corrosion problem. Possibilities of electrolytic corrosion are also being investigated in Canada.

National Lead Co.'s autoclave has been in operating service 4 months during which 1400 tons of ore have been leached. A recent inspection showed no signs of corrosion at or below the pulp level. Above the pulp level there were several deposits of hard mud like material. When these deposits were scraped off, there were indications of pitting corrosion beneath some but not all of the deposits. The majority of the pits were so small or shallow that they were not measured. It was noted during the inspection that the deposits were acidic, testing in the range of pH 5 to 6 with litmus paper. Sulfide content of the ores treated in the pilot plant has been considerably less than those treated in autoclaves at Beaverlodge.

Utility Costs

A summary of average utility consumption figures is shown in Table III along with a rough estimate of the cost of steam and power for the autoclave and

for Pachuca tanks operated with and without pressure applied on top. The leaching conditions shown resulted in 97 pct extraction on La Sal ore.

Steam consumption in the Pachucas was almost twice that for the autoclave, 800 to 820 lb per ton compared with 430 lb. Theoretical heat balances did not corroborate the pilot plant figures for the Pachucas, due to high heat losses from the Pachucas and the quantity of heat expelled in the form of water vapor in the air leaving the top of the Pachucas.

It is estimated that heat losses from the Pachucas due to radiation and convection may be as high as 35 pct of the total heat input. The radiation area per unit volume of pulp in the pilot vessels, of course, is very large (approximately 5 times) compared to commercial size tanks. In commercial mills, a large amount of the heat in the pulp leaving the leach circuit operated at elevated temperatures would be recovered both for reasons of heat economy and to prevent excessive flashing of steam. The steam consumptions at the bottom of Table III are calculated on the basis of recovery of heat from the exit pulp, 250° in the autoclave and 220° in the pressurized Pachucas, down to a temperature of 150°F. Further cooling is not desirable as it would be detrimental to filtration. Were the heat recovery equipment in use in the pilot plant, steam consumption by calculations would be 800 lb per ton for the Pachucas, 660 lb per ton for pressurized Pachucas, and 217 lb per ton for the autoclave. At a steam cost of $0.80 per 1000 lb, a savings in pilot plant steam costs of approximately $0.47 per ton of ore could thus be realized by operation of the autoclave and $0.11 by the pressurized Pachucas. Theoretical figures for a commercial mill indicate steam use for leaching may be about 500 lb per ton for Pachucas, 350 lb per ton for pressurized Pachucas, and 200 to 250 lb per ton for autoclaves.

Power requirements in the autoclave for air compression and agitation are higher than for the Pachucas. Mixing in the autoclave is, of course, very thorough compared to the Pachucas. Although no attempt has been made to determine if the agitation in the autoclave is in great excess, it is felt the agitators, with a total of 15 connected horsepower, would be adequate for a vessel of two or three times the size of the existing one, which has a capacity of 1200 gal.

Assuming: 1) that the previously mentioned mill steam consumption figures are reasonable; 2) that the power requirements from the pilot plant Pachucas are applicable for a commercial mill; and 3) that 40 pct of the pilot plant autoclave power for agitation would be required in a commercial autoclave, then utility costs for the autoclave will be about $0.10 per ton cheaper than for pressure Pachucas and $0.25 per ton cheaper than for Pachucas operated at atmospheric pressure.

To select the best leach vessel for the job, costs of operation must be balanced against other factors such as type of ore to be treated, capital cost, maintenance, space requirements, reagent consumption, filterability of leached pulp, and the variety of ores to be treated.

Pilot plant amenability tests have shown the autoclave to be more versatile than the Pachucas in handling different ores. Where the leach time for best extraction in the Pachucas has varied from 48 to 120 hr, 6 to 7 hr retention time in the autoclave has been adequate for all ores treated. A Pachuca not under pressure has a limited maximum operating temperature. An autoclave permits a fairly wide range of operating temperatures and pressures and leaching conditions can be varied to suit the ore.

Table III. Pilot Plant Steam and Power Costs

Pilot Plant	Pachucas	Pressurized Pachucas	Autoclave
Conditions			
Ore, tons per day	17.4	17.4	11.6
Leach time, hr	48	32	7
Pressure, psig	0	20	50
Temperature, °F	180	220	250
Air, std cu ft per ton ore	6080	3980	1110
Steam, lb (100 psig) per ton	800	820	430
Power for agitation, Kw-hr per ton			12.9
Power for air, Kw-hr per ton	8.7	5.7	1.62
Total power, Kw-hr per ton	8.7	5.7	14.5
Estimated Operations Costs Per Ton			
Cost of steam at $0.80 per 1000 lb, $	0.64	0.66	0.35
Cost of power at $0.012 per Kw-hr, $	0.10	0.07	0.17
Cost of steam and power, $	0.74	0.73	0.52
With Pulp Heat Recovery System, Calculated Figures			
Steam, lb (100 psig) per ton	800	660	217
Cost of steam at $0.80 per 1000 lb, $	0.64	0.53	0.17
Cost of steam and power, $	0.74	0.60	0.34

Pilot plant tests using the Pachucas under pressure have not been extensive. However, available results indicating the advantages of operating at a small pressure on top justify any additional initial investment over Pachucas designed to operate at atmospheric pressure. Actually, pressurized Pachucas will probably be cheaper to build, for although somewhat heavier plates will be required for construction, fewer Pachucas will be required.

As a result of the recent interest in alkaline leaching of ores from the Ambrosia Lake area of New Mexico and the applicability of the process to high lime ores, priority is being given this pilot plant toward further investigation of the variables discussed.

Acknowledgments

John S. Brutlenstein and C. K. McArthur, National Lead Co. Inc., under whose direction the pilot plant program is executed, were very helpful in the preparation of this report through their comments and suggestions. The authors wish to express their sincere appreciation to the AEC for permission to publish the results of this test work.

Neither the Government nor the AEC makes any warranty or assumes liability for any information disclosed in this report.

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Ammonium Carbonate Pressure Leaching of Uranium Ores

By B. G. Langston, R. D. Macdonald, and F. M. Stephens, Jr.

WITH the development of uranium ores that contain substantial amounts of acid-consuming compounds, the alkaline leach has become an attractive method for extraction. Considerable work has been done on both atmospheric and pressure-leaching with aqueous solutions of sodium carbonate and sodium bicarbonate as the lixiviants.[1,2,3] For the treatment of uranium-bearing limestones and other high-lime (CaO) ores, the sodium carbonate leach has proven attractive because it avoids the high reagent consumption incurred by the reaction of sulfuric acid with lime. In addition, the corrosion problems with sodium carbonate are negligible as compared with those encountered in the acid-leach system. The sodium carbonate leach, however, does not yield as high an extraction of the uranium as the acid leach and is not attractive for economic reasons when treating ores that are high in sulfates or sulfides.

Although in the sodium carbonate leach process the bulk of the sodium carbonate can be reclaimed and returned to the system, some reagent is consumed by contact with gypsum, pyrite, and silica. Ammonium carbonate would have no advantage over sodium carbonate with respect to the consumption resulting from the presence of gypsum or pyrite in the ores, but consumption resulting from the reaction of sodium carbonate with silica would be eliminated. It was believed that steam stripping of the ammonium carbonate leach solutions to precipitate the uranium and recover the ammonia would give the process an advantage over the sodium carbonate leach, where sodium hydroxide must be supplied to precipitate the uranium.

Chemistry of the Process

If it is assumed that dissolution of uranium in the ore by an ammonium carbonate solution forms ammonium uranyl carbonate, the following equations express the chemistry of the process:

$$9(NH_4)_2CO_3 + U_3O_8 + 1/2O_2 + 9H_2O \rightarrow 3[(NH_4)_4 \cdot UO_2(CO_3)_3 \cdot 2H_2O] + 6NH_4(OH) \quad [1]$$

$$NH_4(OH) + NH_4HCO_3 \rightarrow (NH_4)_2CO_3 + H_2O \quad [2]$$

$$(NH_4)_4UO_2(CO_3)_3 + \text{heat} \rightarrow 4NH_3(\text{gas}) + 3CO_2(\text{gas}) + UO_3 \cdot 2H_2O(\text{ppt}) \quad [3]$$

Because, at atmospheric pressure, ammonium uranyl carbonate decomposes at 212°F, pressure is utilized in the leaching step to minimize the loss of ammonia and carbon dioxide. In addition, to obtain maximum extraction of the uranium from many of the ores, which contain both quadrivalent and hexavalent uranium, pressure facilitates oxidation to the readily soluble hexavalent state in the presence of free oxygen. Although potassium permanganate is an effective oxidizing agent in the ammonium carbonate pressure leach, air is equally effective and much less expensive.

Equation 2 is of interest because ammonium bicarbonate is not required in an ammonium carbonate leach, as is sodium bicarbonate in a sodium carbonate leach. The formation of free ammonium hydroxide within the concentrations obtained in this study had no adverse effect on the dissolution of uranium.

The precipitation of the uranium from the pregnant solution, Equation 3, involves passing steam through the solution, heating it to approximately 212°F, and serving as a sweeping gas to aid in the removal of ammonia and carbon dioxide. Air can be employed as a substitute for steam as a sweeping gas.

The Integrated Plant

A series of five pressure-leaching towers 10 ft high with an inside diameter of 4 in. were fabricated for study of the process variables. Fig. 1 is a photograph of the towers and the countercurrent washing and precipitation tower that was added later to give an integrated plant for evaluation of the unit processes required for both the extraction and recovery of uranium.

Fig. 2 is a flowsheet of the process as visualized for a pilot-plant operating at a feed rate of 12 tons per hour. Although other modifications of the flowsheet might be employed, for the purpose of demonstrating an integrated system, one utilizing a dry grind is shown.

Development of the Leaching Conditions

To determine the amenability of high-lime ores to an ammonium carbonate pressure leach for the extraction of uranium, temperature, pressure, strength of solution, and the amount of oxidation required to convert the quadrivalent uranium to the hexavalent state were considered.

Nine different ores were studied either by small-scale testing or by operation of the pressure leaching towers, but the major emphasis was placed on three of the ores that contained varying amounts of lime (CaO). Table I gives the chemical analysis of these three ores.

Because over 85 pct of the uranium was present in the −200-mesh fractions when the ore was

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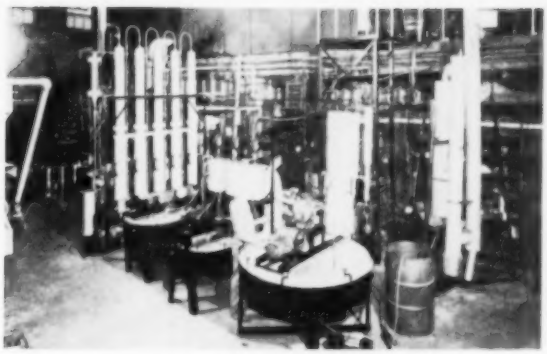


Fig. 1—Integrated plant for the extraction and recovery of uranium by the ammonium carbonate pressure leach process.

ground to pass a 100-mesh screen, it was believed that grinding to a finer particle size would not materially affect the leaching characteristics of the ore. For most ores a slurry with a 50 pct pulp density was sufficient to prevent classification in the towers.

Temperature: A series of tests was run in the towers at temperatures of 185, 225, and 250°F. A pressure of 90 psig and a solution containing 98 g $(NH_4)_2CO_3$ and 54 g NH_4HCO_3 per liter were chosen arbitrarily, based on preliminary test runs in a batch autoclave. In addition, to provide for oxidation of any quadrivalent uranium in the ore, 1500 cu cm of air per min were passed through the towers. This was the smallest flow rate that could be maintained without plugging the air line with slurry. Fig. 3 shows the effect of temperature and time on the extraction of uranium by the ammonium carbonate leach. The primary effect of temperature was the rate of dissolution of the uranium. The leach temperature had little effect, if any, on the maximum extraction of uranium from the ore; in each case about 93 pct was extracted. However, as the temperature was increased from 185 to 250°F the time required for maximum extraction decreased from 375 to 150 min.

Pressure: A series of tests was run varying the pressure from 80 to 115 psig. A temperature of 225°F was chosen to obtain comparative data as to the effect of pressure on the dissolution of uranium, since at 250°F, approximately 92 pct of the uranium was extracted in Tower 1, representing a retention time of 75 min. Fig. 4 gives the data obtained and shows that, although pressure had little effect on the extraction, when extended retention periods were employed, pressure does affect the rate of dissolution of the uranium.

Although the data in Figs. 3 and 4 are believed to be typical of the relation between temperature, pressure, and the extraction of uranium, it is known that the position of the curves varies with each ore, depending probably on the mineralogical state of the uranium-bearing mineral. Fig. 5 shows a comparison of the performance of three ores run through the pressure leaching towers.

Oxidation with air and oxygen enriched air: Tests were run to determine the amount of air required to convert uranium to the hexavalent form. A temperature of 225°F, a pressure of 90 psig, and a solution containing 98 g $(NH_4)_2CO_3$ and 54 g NH_4HCO_3 per liter were employed and the air flow varied from 1500 to 6000 cu cm per min. Within this range, the amount of air passed through the towers had no effect either on the rate of dissolution of the uranium or the final extraction.

An analysis of the exhaust gases from the towers showed that they contained 17 pct O_2 even at the lowest flow rate studied. Thus, it was concluded that a flow rate of 1500 cu cm per min was sufficient for oxidation of any quadrivalent uranium in the ore. However, because the partial pressure of oxygen in the system might affect the rate of oxidation, a test was run with oxygen enriched air. Oxygen

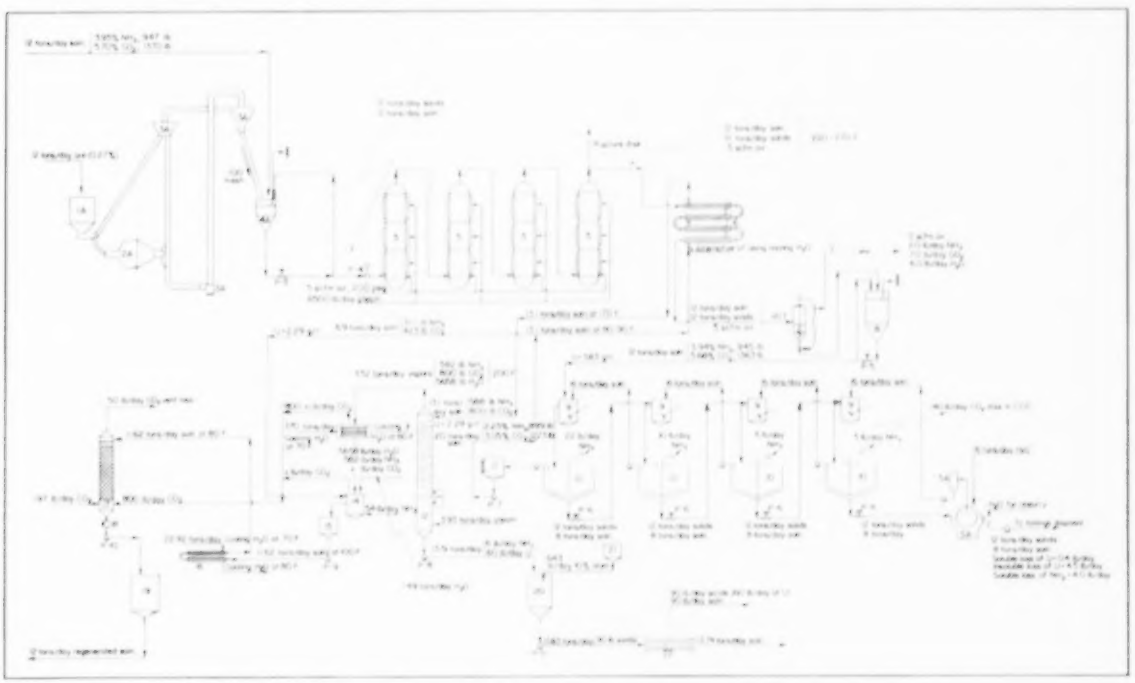
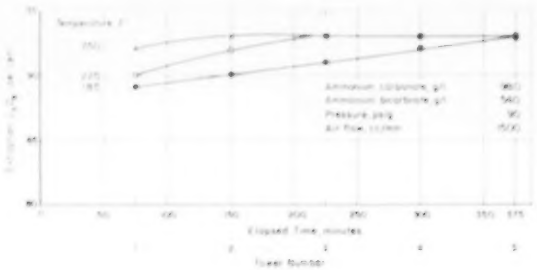
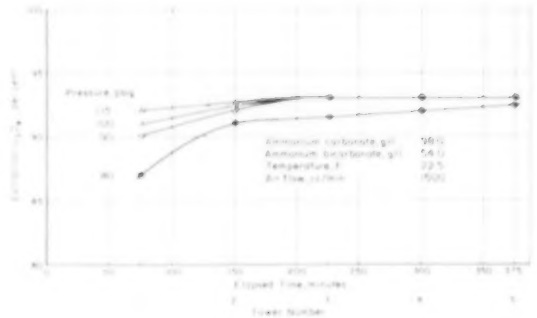


Fig. 2. Process flowsheet for ammonium carbonate leach pilot plant.





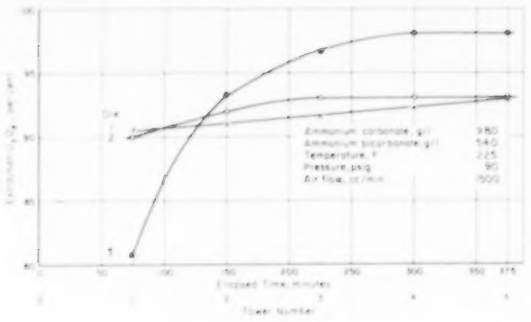


Fig. 3—(upper left) The effect of temperature and time on the extraction of uranium.

Fig. 4—(above) The effect of pressure and time on the extraction of uranium.

Fig. 5—(left) A comparison of the performance of three ores tested in the ammonium carbonate pressure leaching towers.

content of the air was enriched to 30 pct, but addition of this amount of oxygen did not improve either the rate or final extraction of uranium. Although pressures greater than 90 psig or a gas with greater than 30 pct O_2 might have improved the uranium extractions to as much as the 95 pct commonly obtained with a chemical oxidizing agent, further study of oxidation did not appear to be warranted.

Concentration of Ammonium Carbonate and Ammonium Bicarbonate: To evaluate the effect of the concentration of ammonium carbonate and ammonium bicarbonate on the dissolution of uranium, chemical analyses were run on periodic samples of the leach solution from each of the towers. In addition, because the commercial grade ammonium carbonate employed for this work was what is referred to in the literature as *ammonium carbonate of commerce* ($(NH_4)_2CO_3 \cdot NH_4HCO_3$) which decomposes in water to give variable amounts of ammonium carbonate and ammonium bicarbonate, it became necessary to run chemical analyses on the solutions prior to their addition to the repulping tank rather than relying on weighed amounts of the compounds. Fig. 6 shows the data obtained from a series of tests employing varying amounts of ammonium carbonate and ammonium bicarbonate in the leach solution.

Since only small quantities of ammonia and carbonate ions are required for combination with the uranium, then in evaluating the data two factors warrant discussion: 1) total ammonia in the solution contributing to the partial pressure of ammonia in the system and 2) the amount of bicarbonate required to prevent the build up of hydroxyl ions. As shown by Fig. 6, total ammonia content of the solution had a marked effect on the rate of dissolution of the uranium and the maximum extraction. For example, extraction increased from 73.5 to 90 pct in 75 min when concentration of ammonia was increased from 16.3 to 46.2 g per liter. The same change boosted extraction from 86 to 93 pct after the slurry had passed through all the towers.

These data, however, do not indicate any definite effect of the ammonium bicarbonate concentration on the dissolution of uranium. In both tests, represented by Curves A and B, analyses showed that after Tower 1 the solutions contained no ammonium bicarbonate.

To determine whether stabilization of ammonium bicarbonate in solution would improve the dissolution of uranium, the test represented by Curve B was repeated with the addition of 475 cu cm CO_2 per min. Figs. 7 and 8 show that despite addition of carbon dioxide to the system, the rate of dissolution was only improved slightly and maximum extraction was only equal to that obtained in Curve A. These data show that the use of carbon dioxide would permit the use of weaker solutions, but the system appears to have no advantage where the ammonia is recovered by steam stripping.

Precipitation of Uranium From the Ammonium Carbonate Leach Solutions

Uranium can be precipitated merely by heating the solution. This decomposes the ammonium uranyl

Table I. Chemical Analysis of the Ores

	Assay, Pct									
Ore	U_3O_8	V	CaO	Al_2O_3	MgO	C	CO_2	SiO_2	Fe_2O_3	S	L.O.I.
1	0.32	0.02	49.9	1.19	0.62	10.4	37.4	9.13	0.64	0.13	38.9
2	0.12	0.03	5.56	10.0	3.98	0.43	1.41	66.3	2.74	0.20	9.3
3	0.61	0.08	10.8	7.1	2.7	2.6	8.0	61.6	2.56	0.16	12.3

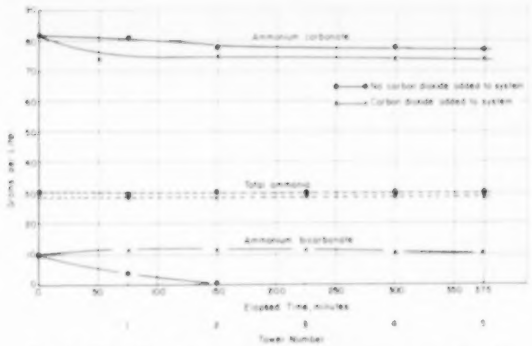


Fig. 6—The effect of concentration of ammonium carbonate and ammonium bicarbonate in the leach solution on the extraction of uranium.

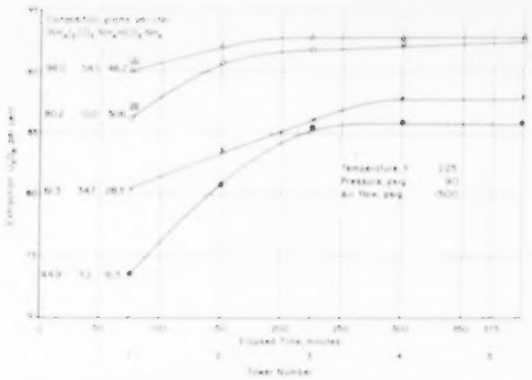


Fig. 7—Concentrations of ammonium compounds in solution with and without carbon dioxide added to the system.

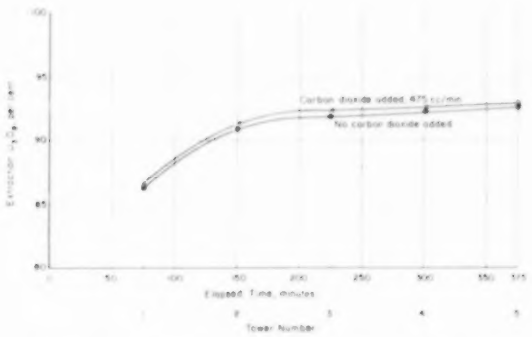


Fig. 8—The effect of the addition of carbon dioxide to the system on the extraction of uranium.

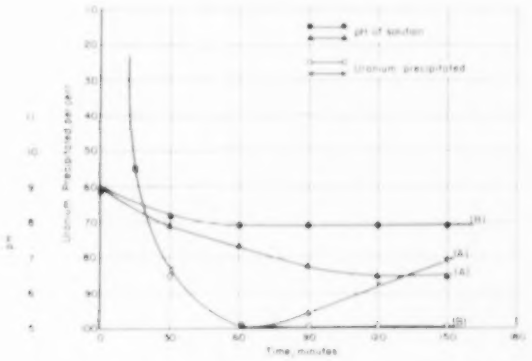


Fig. 9—The effect of time and pH of the solution on the precipitation of uranium by steam stripping.

carbonate and ammonium carbonate-bicarbonate, and expels the ammonia and carbon dioxide, which are then recovered by absorption in a solution brought to a concentration satisfactory for return to the leaching system. The following equations express the chemical reactions involved:

$$(NH_4)_2CO_3(aq) + \text{heat} \rightarrow 2NH_3(g) + CO_2(g) + H_2O(l) \quad [4]$$

$$NH_4HCO_3(aq) + \text{heat} \rightarrow NH_3(g) + CO_2(g) + H_2O(l) \quad [5]$$

$$(NH_4)_4UO_2(CO_3)_3(aq) + \text{heat} \rightarrow 4NH_3(g) + CO_2(g) + UO_3 \cdot 2H_2O(s) \quad [6]$$

$$2NH_3(g) + CO_2(g) + H_2O(l) \rightarrow (NH_4)_2CO_3 \quad [7]$$

In the experimental work, steam was used to heat the solutions and to serve as a sweeping gas. In the operation of the integrated plant, air was substituted for part of the steam. Fig. 9 shows the relation between pH of the solution, time, and the amount of uranium precipitated.

The pH of the pregnant solutions varied from 9.0 to 9.2, depending on the variation in pulp density. In the test represented by the curves A and A', the pH of the solution was not controlled by the addition of fresh solution. As the ammonia was stripped from the solution, the pH dropped, and almost complete precipitation occurred within 60 min at a pH of 7.3. As the pH dropped to below 7, the precipitate began to redissolve. At the time of maximum precipitation, the stripped solution contained 0.005 g U per liter compared with 2.0 g per liter in the pregnant solution.

To determine whether pH of the solution could be employed for operational control when the pre-

Table II. Chemical and Spectrographic Analysis of Precipitate

	Chemical Assay, Pct				Spectrographic Assay, Pct				
	H_2O (250°F)	L.O.I. (1742°F)	U	V	Fe	Ca	Mg	Al	SiO_2
Ore 1									
Air Dried	23.4	—	44.7	0.40	<0.01	0.05	0.01	1.3	1.3
Ignited 1742°F	—	33.2	67.3	0.50	<0.01	0.08	0.02	2.0	2.0
Ore 2									
Air Dried	6.0	—	49.7	0.25	<0.01	0.34	0.5	0.4	3.1
Ignited 1742°F	—	15.0	59.3	0.21	<0.01	0.40	0.7	0.5	3.7
Ore 3									
Air Dried	7.3	—	59.0	0.40	<0.01	0.12	0.04	1.6	1.3
Ignited 1742°F	—	17.0	72.5	0.44	<0.01	0.16	0.05	2.0	1.8

Table III. Typical Uranium and Ammonia Balance

Uranium Balance			
Basis:			
Ore assay uranium, pct		0.52	
Feed rate, kg per hr		13.63	
Extraction uranium, pct		98.0	
Pregnant liquor assay uranium, g per liter		3.36	
Soluble uranium to CCD system, g		816	
Soluble uranium removed as samples, g		14	
Net soluble uranium to CCD system, g		802	
Distribution of Uranium in CCD System:	**Grams**		**Dist. Pct**
Thickener No. 1 overflow: 45.4 liter per hr x 1.5 g per liter x 12 hr	789.6		98.4
Soluble loss: 9.5 liter per hr x 0.11 g per liter x 12 hr	12.6		1.6
Total	802.2		
Distribution of Uranium in Precipitator:			
Loss in barren solution: 50 liter per hr x 0.006 g per liter x 12 hr	3.6		0.7
Over-all uranium loss: Soluble loss + loss in barren solution	16.2		2.3
Ammonia Balance			
Basis:			
Discharge from leaching unit, liter per hr		20.2	
Assay of pregnant liquor, NH_3, g per liter		30.6	
Total NH_3 to CCD system, g		7272	
NH_3 removed by sampling, g		143	
Net NH_3 to CCD system		7129	
Distribution of NH_3 in CCD System:	**Grams**		**Dist. Pct**
Thickener No. 1 overflow: 45.4 liter per hr x 12.8 g per liter x 12 hr	6973.2		98.0
Soluble loss: 9.5 liter per hr x 1.2 g per liter x 12 hr	137		
Total	7110.2		
Distribution of Ammonia in Precipitator:			
Ammonia recovery: 35.2 liter per hr x 15.7 g per liter x 12 hr	6631.7		95.0
Loss in barren solution: 50.0 liter per hr x 0.30 g per liter x 12 hr	180		2.6
Unaccounted loss	161.5		2.3
Total	6973.2		
Over-all loss: Soluble loss + loss in barren solution + unaccounted loss	478.5		6.8

cipitation tower is operated on a continuous basis, a test was run maintaining the solution in the precipitation tower at pH 8 by continuously feeding the pregnant solution to the tower. The curves B and B′ show that by maintaining pH 8, the precipitation tower could be operated on a continuous basis and accomplish almost complete precipitation of the uranium. Although a pH of 7.5 appears to be a critical point with respect to redissolution of the precipitate, it is believed that the critical pH varies with each ore, depending on the salts remaining in the solution after stripping the ammonia.

At the time maximum precipitation of the uranium occurred, more than 99 pct of the ammonia and carbon dioxide had been stripped from the solution.

Composition of the Precipitate: Precipitates were produced from operation of the integrated plant on three ores. Table II gives the data obtained from chemical and spectrographic analysis of these precipitates. These data show that when the precipitates are air dried, uranium content varies from 44.7 to 59 pct. When the precipitates are ignited at 1742°F the uranium content varies from 59.3 to 72.5 pct. As shown by the spectrographic analysis, the variation is caused primarily by solids carry-over from the countercurrent washing circuit. This contamination could have been reduced by employing a clarification filter between the thickener overflow and the precipitation tower. The uranium compound in the air-dried precipitates was identified as $UO_4 \cdot 2H_2O$ by X-ray diffraction. The ignited precipitate was identified as U_3O_8.

Operation of the Integrated Plant for the Extraction and Recovery of Uranium

Because one of the attractive features of the ammonium carbonate pressure leach is the recovery of the ammonia for return to the leaching circuit, a countercurrent decantation washing circuit and a precipitation tower were added to the system. The objective of the program was to demonstrate the uranium and ammonia recovery that could be accomplished in an integrated plant. Although it was not within the scope of this program to actually return the ammonia to the leaching circuit, absorption towers were employed to recover the ammonia from the precipitation tower. Table III gives the uranium and ammonia balance obtained from operation of the integrated plant on Ore 3.

These data show that the soluble loss of uranium from the countercurrent decantation system was 1.6 pct of the uranium in the pregnant liquor and that an additional loss of 0.7 pct was incurred by the barren solution discharged from the precipitation tower. On this basis, the recovery of uranium from Ore 3 was 95.5 pct of the uranium in the feed to the leaching system. In the case of Ores 1 and 2, where approximately 93 pct of the uranium was extracted in the leaching towers, the over-all recovery of uranium was approximately 91 pct of the feed to the integrated plant.

With respect to the ammonia recovery system, the data show that the ammonia lost with the discharge from the countercurrent decantation washing system was equivalent to 1.67 lb NH_3 per ton of dry feed, and that the total loss of ammonia from the system including the loss with the barren solution and the unaccountable loss was equivalent to 5.85 lb per ton of dry feed to the integrated plant.

Conclusions

The data obtained from this study have demonstrated that the ammonium carbonate pressure leach is a technically attractive method for extraction of uranium from high-lime ores.

As in the case of other processes developed for the extraction of uranium from domestic ores, the process does not appear applicable to high gypsum or high vanadium ores. On the other hand, with its low reagent cost for precipitation and the recovery of substantially all of the ammonia, the process appears to have advantage over other alkaline leach processes. In addition, because of these same factors, it is probably competitive with an acid leach of medium-lime ores. At the same time, because an acid leach usually will extract about 98 pct of the uranium from low-lime ores, the acid leach still appears to maintain its advantage. The advantages and disadvantages of the several methods available for extracting uranium from low-grade ores are such that a careful economic comparison should be made for each ore being considered.

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Uranium Recovery by the Solvent Extraction Process

Mills employing the sulfuric acid leaching method for uranium have been confronted with a major problem in recovering uranium from leach solutions, but today, solvent extraction offers a new method of processing these leach solutions. During the past year, the industry has seen the operation of solvent extraction circuits at the Climax Uranium Co. mill of Grand Junction, Colo., the Kerr-McGee Oil Industries Co., mill at Shiprock, N. M., and the AEC Pilot Plant operated by National Lead Co., Inc. at Grand Junction, Colo. The Vitro Uranium Co. constructed and operated a 10 gpm pilot plant and is converting to solvent extraction.

By James D. Moore

IT has been said that the solvent extraction process is rapidly becoming one of the hydrometallurgist's most valuable tools. Chemical and petroleum industries have employed solvent techniques for many years to produce desired purifications and separations; and, although the process has been applied to various phases of the uranium industry for nearly a decade, by comparative standards, it is in its infancy in the field of metallurgy. Solvents are being employed in the purification of crude uranium concentrates to produce high grade uranium products suitable for conversion to reactor grade uranium metal. Another application is in the processing of irradiated reactor fuels.

Until recently, however, application of solvent extraction has been restricted to those uranium products encountered after it had once been recovered as a concentrate from the raw ore. These concentrates may contain upwards of 75 pct U_3O_8 and may be of several types, depending on their chemical composition. Mills producing such concentrates, and particularly those which utilize the conventional sulfuric acid leaching method, have been confronted with a major problem in recovering uranium from the leach solution.

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Older uranium recovery systems

Mills which started operations around 1950 had a choice of two processes. One system requires complete neutralization of the leach liquor to produce a sludge containing not only uranium, but also vanadium, iron, alumina, silica, and other acid solubles. A sodium diuranate is finally produced by precipitation with caustic after dissolution in carbonate.

The second process is known as uranous phosphate precipitation, which involves reduction from the uranyl (+6) state to the uranous (+4) state by the addition of a strong reducing agent, such as powdered aluminum. In this case uranium precipitates as a phosphate, which is later upgraded by hot caustic washes.

Mills constructed more recently have turned to ion exchange recovery processes in either the column or the pulp form. The first system is designed to process clear leach solutions following removal of the leached residue; the second, the pulp system is designed to process the solution in the slime fraction of the leach slurry.

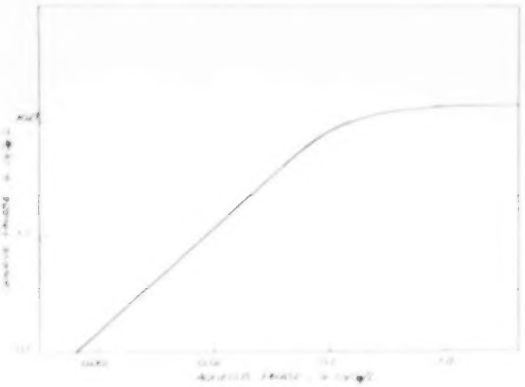


Fig. 1—Typical equilibrium diagram on logarithmic coordinates showing uranium distribution between 0.1 M dodecyl phosphoric acid (DDPA) in kerosene and leach solution.

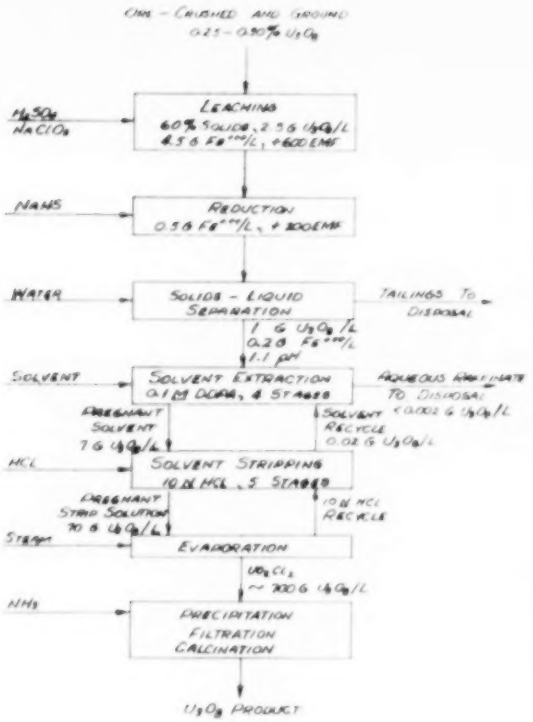


Fig. 2—Proposed uranium recovery process at Vitro Uranium Co., using dodecyl phosphoric acid solvent extraction.

Solvent extraction, a new method of processing sulfate leach liquors

This development has provided a means of circumventing the older, more costly and inefficient precipitation methods; furthermore it is generally considered to be somewhat cheaper from a production standpoint than ion exchange.

Many factors have influenced the development of a satisfactory process for this purpose; a major one is the nature of the uranium sulfate complexes in solution. But their extreme reluctance to form soluble complexes with many of the known organic extractants retarded progress materially. However, research projects continued under AEC contracts by the Dow Chemical Co., Oak Ridge National Laboratories, USBM, National Lead Co., and others, resulted in two general classes of organic solvents which have proven economically suitable; these are the organo phosphoric acids and the alkyl amines. With the successful conclusion of these experiments two mills on the Colorado Plateau, which use sulfuric acid leaching, have converted to the solvent recovery system. Others have the process either in design stages or under consideration.

The Vitro Corp. of America has long held that solvent techniques have a place in the long range routine production of uranium concentrates. Therefore, approximately two years ago, Vitro made a decision to convert its Salt Lake City mill to this process. Results from research and development work being carried on at that time encouraged many to believe that the process could ultimately be applied directly to leach slurries. Such an operation would eliminate the need for expensive dewatering facilities.

At that time, a great deal of information had been developed on the laboratory scale, but there was a substantial lack of data which could be used for plant design. It remained to select the most applicable route and further develop the data necessary for full-scale plant design. This was accomplished by the construction and operation of a pilot plant at the mill site.

Organo phosphoric acid selected as solvent for Vitro pilot plant

There were several important considerations which influenced the selection of an organo phosphoric acid, which had been under study for quite some time by the Dow Chemical Co., and under pilot plant investigation at the Bureau of Mines in Salt Lake City. These factors were: 1) data indicated promise of processing slurries, 2) low first cost for solvent, 3) low solubility in the aqueous phase, 4) high uranium concentration ratios, 5) low over-all chemical costs, 6) much of the work had been done on Vitro's raw ore or leach liquor, and 7) proximity of the Salt Lake City mill to the Bureau of Mines work, which led to a cooperative effort.

The active ingredient or extractant of this solvent is dodecyl phosphoric acid, an ester of 2, 6, 8 trimethyl nonanol, in kerosene, which acts as a diluent or carrier. Although dodecyl phosphoric acid, abbreviated as DDPA, is not a commercial product which can be readily obtained on the chemical market, it is easily formulated from the alcohol and phosphorous pentoxide.

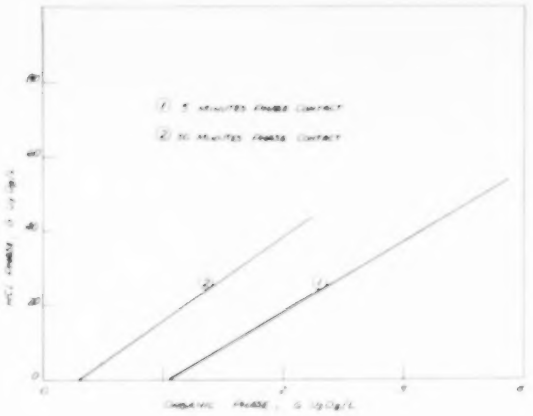


Fig. 3—Equilibrium data for stripping solvent of uranium, showing distribution between the organic and 10 N HCl at two contact times.

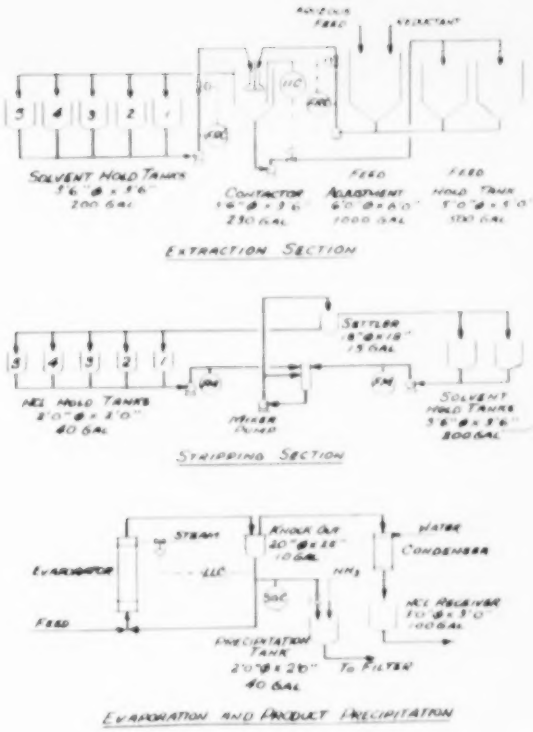
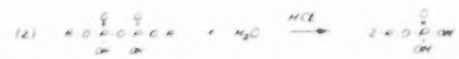


Fig. 4—Solvent extraction pilot plant at Vitro Uranium Co.



The hydrogen atoms are omitted for clarity, and in this case, R represents the dodecyl radical (2, 6, 8 trimethyl nonanol 4).

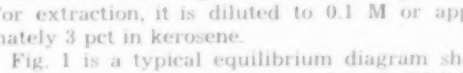
The first reaction is exothermic and is carried out in kerosene diluent. It proceeds rapidly and is generally complete in about 30 min. The hydrolysis reaction proceeds in presence of HCl at ambient temperatures. Yields on the order of 85 to 90 pct are realized, and the product averages 0.9 M DDPA. DDPA has a high affinity and selectivity for uranium, which allows recovery in the solvent at concentrations much higher than in the aqueous feed. For extraction, it is diluted to 0.1 M or approximately 3 pct in kerosene.

Fig. 1 is a typical equilibrium diagram showing uranium distribution between 0.1 M DDPA and representative leach solution. Such curves were extremely useful in predicting the number of theoretical stages for recovery and were further used to guide the piloting investigation. Operation at a 6 or 8 to 1 aqueous to organic volume phase ratio produces satisfactory concentration.

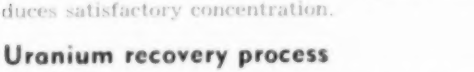
Uranium recovery process

A simplified block flow diagram of the proposed uranium recovery process, including typical operating data which might be expected, is presented in Fig. 2. Ground ore is leached with sulfuric acid at about 60 pct solids. Following the last leach tank, the slurry is treated with a reducing agent to minimize the extraction of undesirables, such as Fe^{+++}. Sodium sulfide, sodium hydrosulfide, or even powdered iron has been used for this purpose, and Fe^{++} is only slightly extracted. Solids-liquid separation is carried out either by a countercurrent decantation system or by filtration, wherein tailings residue is discarded and leach liquor is recovered. This liquor is suitable to process directly in the solvent extraction plant without further treatment. Uranium extraction is carried out in countercurrent fashion in four stages at a 7:1 aqueous to solvent ratio.

The mechanism of extraction is believed to involve the transfer of UO_2^{++} from the aqueous phase for H in the organic phase, according to the reaction:



Uranium is removed from the solvent, for recycle and further uranium extraction, by stripping with strong HCl. Ten normal HCl is required to provide the necessary H to restore the organic and the Cl to produce uranyl chloride, UO_2Cl_2, according to the following:



Further concentration of uranium occurs during this step by maintaining a 10:1 organic to aqueous phase ratio. Equilibrium data for stripping are influenced by contact time and temperature. Fig. 3 is a plot of data obtained during the early part of the work, showing distribution between the organic and 10 N HCl at 5 min and 30 min contact time.

Hydrochloric acid is recovered for recycle by evaporation and condensation, leaving uranium chloride in the heel. This is neutralized with ammonia to produce a precipitate, which is then calcined to drive out NH_3 and NH_4Cl.

It will be noted that the expression, *solvent extraction*, as used here, is not entirely correct. The process described is actually an ion exchange process which might be compared with the ion exchange resin process, the basic difference being in the character of the carrier employed, one a liquid, the other a solid.

The pilot plant

The pilot plant, or perhaps more properly the demonstration unit, was operated primarily for the purpose of obtaining design information and, to a lesser extent, for the purpose of investigating various chemical aspects of the process. Necessary equipment was included to study four-stage countercurrent extraction and four-stage countercurrent solvent stripping. In addition, an evaporator system allowed HCl and uranium product recovery. Fig. 4 is a flow diagram of the pilot plant.

The extraction section: This section is composed of a set of five solvent hold tanks, two aqueous hold tanks, a feed adjustment tank, and the contactor. All tanks are constructed of carbon steel with neoprene lining; the contactor is of the internal mixer-settler design. Conventional gas-liquid dispersion equipment was modified for liquid-liquid contact within the settler vessel. This unit is simply a shrouded impeller, equipped with a feed tube, submerged below the solvent surface in the settling vessel. The 6-in. diam impeller is driven by a ¼ hp variable speed motor at peripheral speeds in the range of 400 to 600 ft per min. It provides the necessary contact and also a means of maintaining the organic phase continuous. It was mentioned earlier that the aqueous to solvent feed ratios were normally maintained in the range of 6 or 8 to 1. However, unless sufficient solvent is recycled to the mixing zone to maintain organic as the continuous phase, serious emulsion or entrainment difficulties can be expected. Therefore, solvent from the surface was recycled down the draft tube.

Raw unclarified leach liquor was treated with sulfide in the adjustment tank, and four-stage countercurrent extraction was simulated by successively contacting this batch with previously prepared solvent held in the solvent hold tanks. Uranium concentrations of a predetermined quantity of solvent was provided in each of four hold tanks corresponding to the feeds to each of the four extraction stages. These concentrations were estimated from the distribution curves, and exact loadings were not critical. By contacting the same batch of aqueous feed with successive batches of solvent, each on a continuous basis, it was possible to reproduce results which were comparable to those of a continuous four-stage system. Uranium extractions well over 99.5 pct have been produced. Interstage data agreed satisfactorily with that obtained on laboratory scale, and stage efficiencies were determined to be on the order of 90 to 100 pct. Barren aqueous was discarded, and loaded solvent was transferred to the stripping section after each cycle.

This system was quite satisfactory for confirming laboratory and Bureau of Mines pilot plant data. It remained to determine contactor and settling vessel

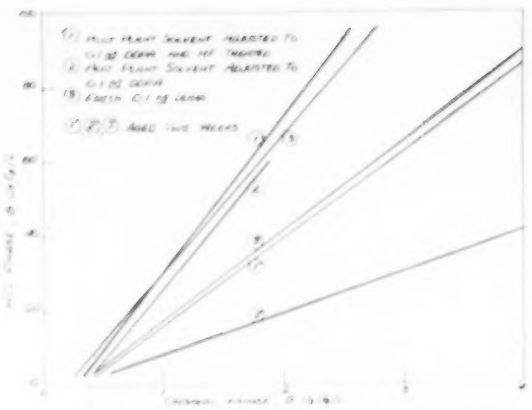


Fig. 5—Distribution of uranium between 10 N HCl and 0.1 M dodecyl phosphoric acid, showing the aging effects on three samples.

capacities to arrive at design factors. The capacity of the vessel was considered to be that maximum aqueous feed rate which could be satisfactorily separated from the solvent associated with it. Variations from equilibrium were considered to determine the contactor capacity. It was evident after a few runs that increasing the feed rate beyond 10 gpm would require discontinuing the four-stage operation, since the total run time per stage was reduced to an inconvenient figure. Furthermore, it was unnecessary to continue the four-stage operation, since both physical and chemical capacity considerations could be included in the study of a single stage at higher feed rates. Therefore, all solvent was adjusted to the same uranium concentration and capacity studies continued. The capacity of the 3 ft 6 in. diam vessel was reached at approximately 12.5 gpm. This gave a figure of 1.3 gpm per sq ft based on the cross sectional area. Since there was no indication of limiting contactor capacity, the contactor was moved to the 6 ft-diam feed adjustment tank. Feed rates were increased to a maximum of 40 gpm, whereupon other factors were limiting, including the feed pumps and the solvent flow meter. However, appearance of the solvent indicated this was near the tank capacity. This rate checked previous findings and gave a figure of 1.4 gpm per sq. ft.

Stripping section: Stripping of DDPA was originally believed to be only slightly more difficult to accomplish than the extraction. This section was conceived to operate similar to the extraction section, in that semi-continuous operation could reproduce continuous results. Five HCl hold tanks and two solvent hold tanks were provided in this case, together with a pump mixer system designed to provide approximately 5 min contact time. Data obtained from the first few runs indicated insufficient contact time had been provided; therefore, a four-stage, and later a five-stage, mixer settler system was installed. This unit was operated in a continuous countercurrent fashion and provided about 1 hr contact time per stage. With extended time, satisfactory stripping results were obtained. Although the system varied somewhat, it appears that design should be based on a 1-hr contact time at a temperature in the range of 25° to 30°C. To provide this relatively long hold time is not a serious problem, since the total volume

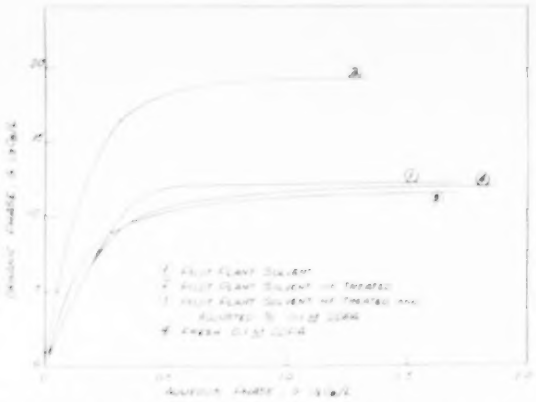


Fig. 6—Distribution of uranium between reduced liquor and dodecyl phosphoric acid, showing only slight differences between HF treated and freshly prepared solvent.

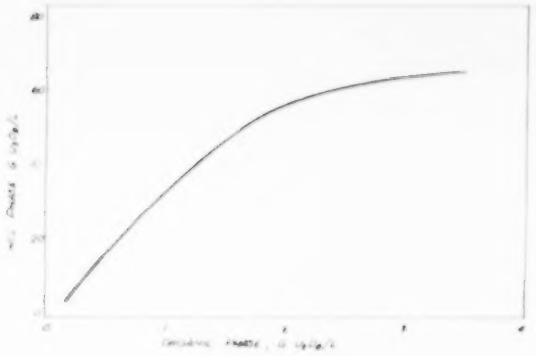


Fig. 7—Distribution of uranium between 10 N HCl and 0.1 M dodecyl phosphoric acid, showing equilibrium encountered with HF treated sample.

of both phases to be handled in this section is approximately one-seventh of the fresh aqueous feed to the plant.

Extractive efficiency of solvent

As successive cycles of extraction and stripping were carried on, it became apparent that the solvent was losing its extractive efficiency, and, also, it was becoming increasingly difficult to strip. The decreased extraction efficiency was expected, inasmuch as previous work had determined that such materials as titanium, and perhaps some of the rare earths, were not removed by HCl stripping. This led to a laboratory investigation of the solvent, wherein it was discovered that sufficient kerosene diluent had been lost by evaporation to substantially increase the DDPA concentration. This concentration increase had masked the poisoning effect of the contaminants and had caused the apparent uranium loading to remain relatively constant. By treating this material with dilute HF it was restored to its original state. Analysis of the precipitate produced during this treatment indicated titanium had been the major contaminant, along with substantial quantities of thorium and, surprisingly, uranium, probably picked up as U^{+4}.

Aging Effect: At approximately the same time, it was speculated that stripping had been affected by aging of uranium bearing solvent. It so happened that the nature of the pilot plant operation required considerable quantities of loaded solvent to stand for periods of several days before stripping could be completed. An investigation of this was carried out, and results are demonstrated by Fig. 5. Three samples of solvent were compared: 1) pilot plant solvent adjusted to 0.1 M DDPA in kerosene and HF treated; 2) pilot plant solvent adjusted to 0.1 M DDPA in kerosene; and 3) fresh 0.1 M DDPA in kerosene. Each was contacted with leach liquor to produce reasonable loadings, and then one-half of each sample was subjected to successive contacts with fresh HCl. The remaining half of each solvent sample was allowed to stand for two weeks and then given similar contacts with HCl. It was apparent that more stages were required to strip aged samples, and that the contaminated sample was most seriously affected. A check was made to determine if the fluoride treatment had resulted in any detrimental effect on the extraction characteristics of the solvent, but data from equilibrium tests shown in Fig. 6 indicate only slight differences between treated and freshly prepared materials. Fig. 7 demonstrates the type of stripping equilibrium which was encountered with the treated sample. It was concluded from these studies that solvent poisoning reduces extraction efficiency, while aging makes the solvent more difficult to strip.

As a result of these studies, a life test was started on a continuous basis in the laboratory, using poisoned solvent after treatment with HF. Excellent extraction and stripping results have been obtained; and, as of this writing, 30 cycles have been completed with no apparent effect on either extraction or stripping. Further operation of the pilot plant has confirmed the effect of aging, which was easily eliminated.

Pilot plant evaporator equipment

The evaporator equipment, as installed, was operated to recover 10 N HCl and a bottoms product averaging 250 g U_3O_8 per liter. This unit is the conventional thermo-syphon type system, and recovery of 10 N acid was limited to approximately 65 pct. At the sacrifice of low HCl concentration in the condensate, uranium concentrations in the bottoms were pushed to well over 600 g U_3O_8 per liter, and indications are that this can safely be pushed to 700 gpl. To overcome the HCl recovery problem, a drying unit employing sulfuric acid should be considered for removal of moisture from the vapor stream.

Evaporator bottoms have been neutralized with anhydrous ammonia to precipitate a uranyl hydroxide product running 75 to 85 pct U_3O_8 after calcination at 600°C.

In conclusion

It is our opinion that solvent extraction processes will become even more valuable in the production of uranium products. The inherent flexibility and wide choice of reagents offer a seemingly unlimited number of combinations and possibilities for purification of uranium from ores to final high grade salts.

Manganese From Low-Grade Ores

by J. Y. Welsh and D. W. Peterson

A NEW and unique process for the hydrometallurgical extraction of manganese has been developed from a laboratory concept to full scale plant production within the past five years. The process, known as the *Dean-Leute Ammonium Carbamate Process*, has been applied with proven success by Manganese Chemicals Corporation to the low grade manganiferous ores of the Cuyuna Range in Minnesota, and offers a real aid to the critical problem of a stable and assured supply of metallurgical manganese for our steel industry, in the event of a national emergency. The importance of a source of manganese from low-grade domestic deposits is evident from the fact that 90 pct of the managanese ore used in this country must be imported.

The present plant is located at Riverton, Minnesota, and is scaled to process some 200 tons of raw ore per day. A plant of this size can be viewed as a practical pilot plant for metallurgical requirements. On the other hand, it represents a full scale plant for the production of manganese for specialty uses. Further, the carbamate process produces a very high purity $MnCO_3$, which is an ideal starting material for a wide variety of manganese compounds. The low cost of the carbonate produced by the process, plus advantages in subsequent processing, make it possible for this product to compete successfully with other processing methods in the production of manganese compounds for specialty applications.

The chemistry of the *Dean-Leute Ammonium Carbamate Process* is unique. The process is based on the fact that manganous oxide, MnO, forms a soluble complex in aqueous solutions containing high concentrations of ammonia and carbon dioxide, and that this complex functions as an intermediate in the combination of MnO with CO_2 to form $MnCO_3$.

At the ammonia and carbon dioxide concentrations employed—about 18 moles per liter NH_3 and 3 moles per liter CO_2, the NH_3–CO_2–H_2O equilibria is displaced from the carbonate to the carbamate

J. Y. WELSH and D. W. PETERSON are Director of Research and Plant Superintendent, respectively, Manganese Chemicals Corp., Minneapolis. Paper presented at AIME Annual Meeting, New Orleans, February 1957.

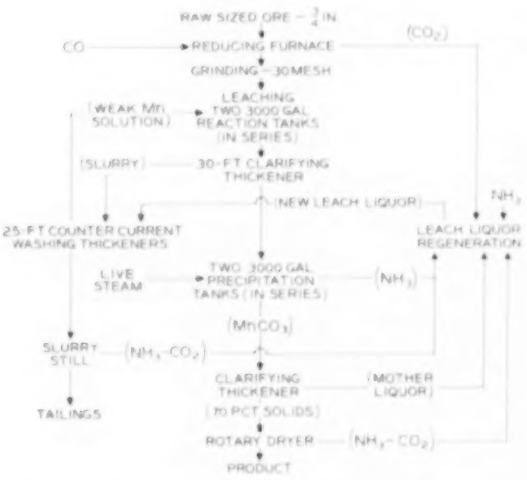


Fig. 1—Flow sheet of the Dean-Leute Ammonium Carbamate Process.

By the Ammonium Carbamate Process

Proven in production, this process promises high purity manganese compounds for specialty applications, from ores of the Cuyuna Range.

structure as follows:

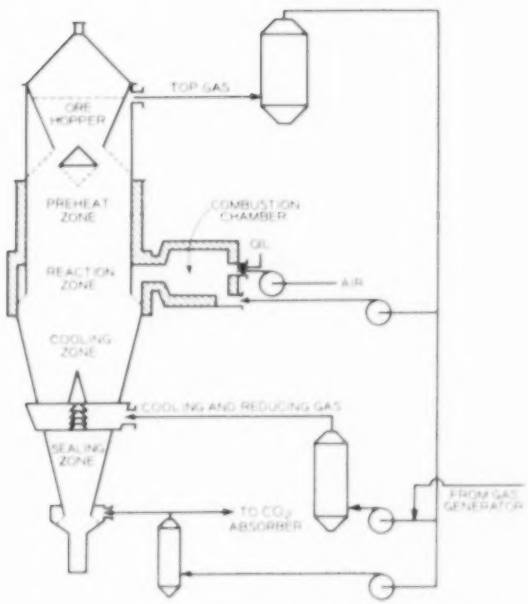


Fig. 2—Shaft-type furnace used for reduction of the ore.

Dr. R. S. Dean's initial work on this system (covered by U. S. Patent 2,608,463, August 26, 1952) showed the MnO to be complexed with the carbamate ion. He postulated the following structure:

The complex, when broken down by heat and/or by loss of NH_3, results in the precipitation of manganese as a carbonate.

The initial chemical step in the overall process is the reduction or decomposition of the manganese compound within the ore to MnO. The chemistry of the carbamate leach liquor imposes a secondary consideration at this point, since any iron present at a reduction level equivalent to FeO is also solubilized by the leach liquor in an analogous manner to MnO. This makes it necessary to control the ore reduction step in such a way that iron is maintained as insoluble Fe_3O_4 while manganese is completely reduced to MnO.

With proper control at this step, it has been found possible to hold the iron level in the final product to 0.10 pct or less. It is evident, therefore, that the reduction of the ore is one of the most critical steps in the entire process.

The leaching step is carried out by carefully proportioning ground, reduced ore and carbamate leach liquor into agitated tanks. The formation of the carbamate complex gives off heat, sufficient to raise the

temperature of the reacting slurry about 0.3°C for each gram per liter of manganese leached. This is particularly important from a processing point of view since, as previously indicated, the complex is unstable with respect to heat and careful control must be exercised to hold the temperature of the reacting slurry within proper limits. Some heat is desirable because it speeds up the solution of the MnO, but too high a temperature at this point will cause the complex to break down prematurely to $MnCO_3$, and of course, any $MnCO_3$ formed in the slurry cannot be reclaimed. It is of particular interest that a *snowballing* type of situation can develop during the leaching step if MnO is present in considerable amounts over that which can be held in solution at slightly elevated temperatures. Under these circumstances, the first MnO taken into complex raises the temperature, resulting in a faster reaction evolving more heat—until a precipitate of $MnCO_3$ eventually results. This permits more MnO to be dissolved. Thus, a leaching and precipitation process can continue simultaneously, with the carbamate complex functioning merely as a transitory intermediate. The reaction is terminated when either the MnO is depleted or the CO_2 component of the leach liquor becomes so low that a complex can no longer form. A laboratory investigation of the above problem has shown that 1 liter of full strength leach liquor can dissolve and *reprecipitate* as much as 110 g Mn as Mn^{++}, while maintaining a final soluble manganese concentration of about 55 g per liter as Mn^{++}.

The chemistry of the leaching step involves one other critical control. The nature of the complex requires that the manganese exist entirely as MnO, and any inadvertent oxygen pick-up by the reduced ore, no matter how slight, must be counteracted in order to avert a sharp reduction in leaching efficiency. Reduction of any excess oxygen is brought about in two ways. First, any soluble iron in the leach liquor (present as the FeO complex) acts as a mild reducing agent. This has the double benefit of removing the iron as insoluble $Fe(OH)_3$ and assisting in the solution of manganese. Second, ammonium sulfide, in which the sulfide ion acts as a reducing agent, is added in controlled amounts. If the ore grinding circuit is carefully balanced to prevent excessive reoxidation of the reduced ore, the addition of ammonium sulfide can be held to a very low level, usually on the order of 0.1 pct or less. Poorly reduced ore or reoxidized ore requires higher sulfide, with the added disadvantage that some iron is also reduced to the soluble state making iron control difficult.

The manganese is recovered from the soluble complex by heating the solution with live steam to 55° to 65°C. The combined effect of elevated temperature and lower ammonia concentration—reduced to about 10 to 11 moles per liter—breaks down the manganese complex and permits the precipitation of virtually all the manganese. The precipitate formed varies with the temperature at which it is precipitated. Below 55°C the precipitate tends to form a hydrated carbonate. Above 55°C it forms a well crystallized manganese carbonate having the usual rhodocrosite crystal structure. The hydrated form, if precipitated at a sufficiently low temperature to be stable, tends to be colloidal, but will convert to the crystallized form when heated. The hydrated product is resoluble in leach liquor, whereas the crystallized carbonate cannot be redissolved. In practice, it has been found that careful control of the precipitation conditions is necessary to maintain uniform characteristics of the final product.

Table I. Furnace Operating Conditions

Peak temperature in reaction zone	750-900°F
Combustion chamber gas temperature	750-900°F
Combustion chamber gas analysis	16 pct CO_2 1 pct CO 83 pct N_2
Cooling & reducing gas analysis (saturated with H_2O at 80°F)	16 pct CO_2 8 pct CO 2 pct H_2 74 pct N_2
Top gas analysis	20 pct CO_2 78.5 pct N_2

The $MnCO_3$ produced by the ammonium carbamate process has a basic particle size of 1 to 4 μ and takes the form of a light tan, free flowing powder containing more than 46 pct Mn against a theoretical value of 47.8 pct. The difference between the actual and theoretical values is primarily due to the presence of water and ammonia. Both of these can be diminished by a calcining treatment. Other impurities combined amount to less than 0.8 pct.

The flow diagram of the process is shown in Fig. 1.

Special Process Equipment

There are two phases of the plant process that are worthy of special consideration.

1. A consideration of the reducing furnace, as its operation relates to the manganese ore of the Cuyuna Range.

Most of the Cuyuna Range ores amenable to the process are manganiferous iron ores, with very small and scattered deposits of ferrugenous manganese ores being found from time to time.

A typical ore feed to the plant will assay 9 to 10 pct Mn and 25 to 28 pct Fe. The manganese occurs primarily in the pyrolusite form and, infrequently, as rhodochrosite, and the iron occurs almost exclusively as hematite. The initial step, therefore, requires the reduction—or decomposition in the case of rhodochrosite—of the manganese in the ore to MnO. This reduction is exothermic with respect to MnO, and Fe_2O_3, releasing about 11.6 Btu per lb of ore per 1 pct of Mn, and 0.65 Btu per lb of ore per 1 pct of Fe. As is seen, the heat released by the manganese reduction is 18 times that of the iron reduction, and must be reckoned with very carefully as the per cent manganese increases. It is necessary to prevent overheating of the ore bed and consequent overreduction of the iron below the Fe_3O_4 level, in which state it becomes totally or partially soluble in the carbamate liquor along with the manganese. It is possible, also, in the event of excessive temperature, to form a manganese-iron spinel which is insoluble in the carbamate solution. The equilibrium conditions relative to temperature and gas constituents which are necessary for the reduction of manganese, while maintaining the iron at the Fe_3O_4 level, have been summarized and discussed in several reports[1] and will not be discussed here.

The reduction step is carried out in a shaft-type furnace, Fig. 2, with a capacity of about 10 tons per hr. The diameter of the reaction zone is 9 ft and the furnace is roughly 46 ft long, tapering from 9 ft to 18 in. in the lower 16 ft of the shaft. The design is similar in many respects to the furnace described by F. D. DeVaney.[2]

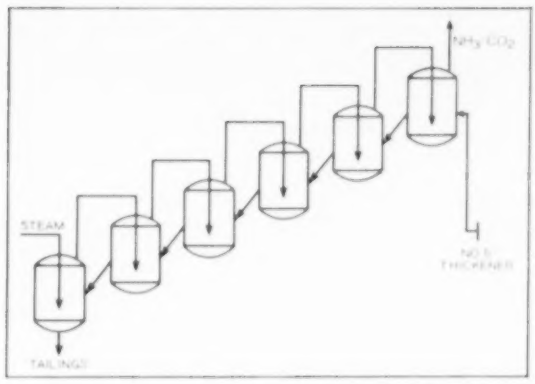


Fig. 3—Six tank slurry still with liquid and vapor phase connections.

Theoretically, the reduction reaction should supply all the heat necessary to replace normal losses without the addition of external heat, but in practice it has been found that it is necessary to provide about 70 to 90 Btu per lb of ore from the combustion of fuel oil to compensate for nonuniform gas-ore contact. This is reflected also by the increase in total heat transfer blow-rate from 9.3 cu ft per lb of ore theoretical to 12 cu ft per lb practical. Other furnace conditions, drawn from operating practice, are summarized in Table I.

Reducing gases are manufactured at the plant in a Wellman-Galusha Gas Producer and are diluted with recirculated top gas to the desired CO level. The top gases are drawn off through a collector manifold at 200° to 250°F. These gases are then scrubbed and cooled and recirculated through low pressure blowers back into the furnace at various levels for cooling and sealing. A portion of these top gases are diverted to the leach liquor regeneration circuit.

II. A consideration of the slurry still and the characteristics of the NH_3-CO_2-H_2O system involved.

The problem of stripping the NH_3 and CO_2 from the spent ore slurry, containing about 60 pct solids, presented a difficult engineering problem. Conventional distilling columns could not be efficiently employed because of the heavy ore which, unless vigorously agitated, would settle out and block or hinder the required vapor and liquid flow patterns.

Distillation analysis indicated that a distilling column with as few as five theoretical plates could strip practically all of the NH_3 and CO_2 from the solution. The low number of theoretical plates required led to the conclusion that a series of agitated tanks with suitable liquid and vapor phase connections would be a practical solution. With the technical aid of the Mixing Equipment Co., a six tank slurry still was designed, as shown in Fig. 3.

A 60 pct slurry is fed into the top tank at the rate of 27 gal per min. The still also handles an additional quantity of NH_3—CO_2 solution amounting to about 12 gal per min in order to maintain a material balance in the process.

The still operation has proven quite efficient and substantially trouble free. The NH_3 concentration in the liquid phase of the discharge slurry is about 0.5 g per liter and amounts to an NH_3 loss of less than 300 lb per day.

Potential of the Carbamate Process in the Metallurgical Field

Plant operation to date has shown that the ores of the Cuyuna Range can be processed by the *Dean-Leute Ammonium Carbamate Process* without difficulty and with an extraction efficiency of at least 70 pct. Also, successful conversion of the carbonate to Mn_3O_4 pellets has been carried out, following procedures similar to those employed in the taconite process. The pelletized product, which meets the physical requirements of government stockpiling specification, contains about 65 pct Mn, 3 pct SiO_2, and 1 pct Fe.

If a large plant were designed to supply 25 pct of our country's total requirements, and if recovery of iron from manganiferous ores were taken into account along with the exceptional purity of the product, it has been estimated that the process could produce manganese at a cost in the range of present market prices for foreign ores.

Some of the more important specialty applications include paint dryers, dry batteries, ferrites, corrosion-resistant coatings, nonferrous alloys, cathodic protection, electrode coatings, animal feeds, fertilizers, and general laboratory and plant chemicals.

The carbonate, by controlled calcining or roasting conditions, can be converted to all of the manganese oxides, and of course most manganese salts can be prepared readily from the appropriate acid. The carbonate can serve also as a suitable feed for the production of electroyltic manganese dioxide or electrolytic manganese metal.

Of particular interest at the present time is the production of a special dry battery grade manganese dioxide by chemical means. Such a method is of interest because of the favorable economics, as compared to the electrolytic manganese dioxide, which is now in general use. Manganese carbonate produced by this process shows unique features as a starting chemical, and the manufacture of high grade battery dioxide comparable to electrolytic dioxide has been on a production basis for over a year.

The use of the product of this process either as the carbonate or an oxide in the production of ferrite bodies is also of interest. This use requires high purity manganese, and represents a rapidly expanding market which in many phases is still in the research stage. Experimental work has shown that the $MnCO_3$ can be converted to Mn_3O_4 in a finely divided free flowing form which contains as little as 0.05 pct total alkalis and alkaline earths. If required, silicates can also be lowered from a normal level of about 0.15 pct to 0.01 pct or less. A high purity Mn_3O_4 is now available on a production basis.

Laboratory work has been completed on a variety of high purity chemicals using $MnCO_3$ as a starting material. This work is presently in the pilot plant stage.

It can be said that the ammonium carbamate process has been successfully proven in production. As is stands today, this process marks the start of a new industry in the field of high quality manganese compounds for specialty uses.

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New Horizons for Lithium

by P. E. Landolt

BEFORE World War I, and even prior to World War II, lithium was considered among the rare elements. Mining was limited to exploitation of a few well selected sources of rich minerals recoverable by hand cobbing methods. Within the past five years the situation has changed radically.

While the Black Hills area of South Dakota is still an important source of lithium minerals, many new sources have been explored and developed, principally in Canada, North Carolina, and Southern Rhodesia. The prime raw material for lithium recovery is spodumene.

In the tin-spodumene belt in North Carolina two large chemical plants are supplied from spodumene ores mined by open pit methods—Foote Mineral Co. and Lithium Corp. of America Inc. A number of other companies, among them Basic Atomics Inc. and National Lithium Co., have explored this area and control considerable acreage. The tin-spodumene belt extends some 35 miles, from Lincolnton, N. C., to a point in South Carolina, just south of Kings Mountain, N. C. Width of this mineralized area varies from 2 to 14 miles.

Canada has become the source of a vast amount of lithium minerals, principally spodumene. The Val d'Or area of northwest Quebec is being mined by Quebec Lithium Corp., which operates a flotation mill to treat at least 1000 tpd averaging 1.25 pct Li_2O, upgraded by froth flotation to over 4 pct.

In the province of Manitoba a number of locations show substantial quantities of spodumene. Principal areas are Cat Lake, Bernic Lake, and Herb Lake. Substantial showings of lithium-containing pegmatites have been reported in Ontario also.

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This paper was presented at the 1957 Annual Meeting.

From all observations to date, the vicinity of Yellowknife, Northwest Territory, north of Great Slave Lake, appears to have a most prolific amount of spodumene. An extended exploration and drilling program carried on during the past 12 to 18 months has revealed pegmatite dikes far richer than those found or developed in other areas.

Ore reserves

How extensive are the various reserves? At best ore values can only be indicated. With a thorough drilling program, *measured* or *proven* ore can be calculated. Beyond that, ore possibilities may be estimated as *indicated* and *inferred*. Experience of recent years has shown that tonnages actually mined will at least equal if not exceed the *measured* ore predicted.

From a review of published and other available material, the situation in the U. S. and Canada would appear to be as follows:

Region	Explored Reserves, Tons	Li_2O Pct
United States		
Black Hills, S. D.	3 to 5 million	1.5 +
North Carolina	100 million	1 +
Canada		
Quebec	20 million	1 to 1.5
Manitoba	15 to 20 million	1 to 2
Northwest Territory (Yellowknife)	100 million	2 +

It should be remembered that these rough tonnage figures are shown to demonstrate the amounts of raw material that may be expected to be mined commercially. These ore reserves will adequately support growing lithium compound production.

It is possible to produce a high grade spodumene concentrate (5 to 6 pct Li_2O) by means of heavy media separation using ferrosilicon as the densifying agent. The method has the advantage of requiring a crushing operation to only $-1\frac{1}{2}$ in. to $-\frac{1}{2}$ diam, depending on the size and free-separation of the spodumene crystals or crystal aggregates. However, the −10 mesh material has to be removed before concentration—a considerable loss of lithium-bearing material. Furthermore, to obtain a substantial throughput, the concentrate economically produced contains 4 pct + Li_2O.

Froth flotation, with crushing and grinding to about −48 mesh, produces a good concentrate. Here also, to make an optimum production a concentrate of 4 pct + Li_2O would be obtained. Output would be sharply decreased by producing 6 pct Li_2O.

In heavy media concentration a recovery of 75 pct ± of the lithium-bearing material can be made. By froth flotation about 65 to 70 pct of the lithium-bearing material is recovered.

There would be considerable advantage in applying heavy media techniques to bulk recovery of the lithium-bearing material. By combining the −10 mesh reject with the heavy media concentrate, and grinding to proper mesh, flotation can be more effectively treated. Accordingly the investment in concentrating equipment can be greatly reduced. Overall recovery from ore to finished concentrates would still be about 70 pct, but a concentration of at least 5 pct Li_2O could be expected.

The objection to such concentrating methods, particularly flotation, is the high cost of plant and high cost of operation, which increase the unit cost of Li_2O delivered to the chemical plant for recovery of lithium. From one ton of ore, containing 1.5 pct Li_2O, mined at $2.50 per ton (avg of open pit and underground mining), costs are:

Per unit Li_2O	$1.67
Per pound Li_2CO_3 equivalent	$0.033
Per pound Li_2CO_3 equivalent on direct recovery from ore	$0.050 (65 pct yield)
Per pound Li_2CO_3 equivalent in 5 pct Li_2O concentrates	$0.104
Per pound Li_2CO_3 equivalent from concentrates	$0.16 (65 pct yield maximum)

Direct ore treatment

At its Bessemer City plant, Lithium Corp. of America Inc. has fully demonstrated the practicability of direct ore treatment, which appears to offer considerable advantage. However, this necessitates a chemical plant adjacent to the mine. Where shipment of such raw material is necessary, only concentrates can be shipped because of the costs of transportation.

It is certain that whatever concentrates are produced in Canada, Africa, or points some distance from the mines, the unit cost of Li_2O will be high, and with attendant losses in the extraction plant, a high unit cost of raw materials will be reflected in the end products. Such raw material costs would be 25¢ to 40¢ per lb lithium carbonate or equivalent.

Growth of lithium industry

Table I, the compilation published by the USBM, shows an annual consumption of lithium products in the U. S. in 1935 to 1939 of approximately 300,000 lb (as lithium carbonate). It is estimated that in 1956 production will exceed 30 million lb, roughly 100 times the consumption 20 years earlier.

What can be expected for the next ten years? Ordinarily an annual increase of 4 to 8 pct could be anticipated. To widen the use of lithium products substantially beyond present uses, costs of production must be greatly decreased. Considerations basic to this requirement may be summed up as follows:

1) Adequate reserves of lithium minerals that are of mineable quality and well located;

2) Better methods of winning lithium from its ores than the conventional methods now in use; and

3) Operations on a large enough scale to permit lowest costs, e.g., the mining and treatment of 1000 tons per 24 hr.

Table II shows approximate capacity of the four producing companies in the U. S. in terms of lithium carbonate or its equivalent. In the past ten years this has been expanded about ten times.

Consumption of lithium products

In Table III estimated figures on total consumption are broken down to show consumption for specific uses or industries. Exact figures are not reported or not available on industrial uses, and quantities for defense requirements are usually classified information. However, the figures presented indicate the distribution of these products.

It is reasonable to expect that demonstrated industrial uses will continue to increase as the industries expand. A vast amount of research will generate further uses. Predictions on market increases are hazardous, but during the next few years industrial demand in the U. S. should approximate the present available capacity. Accordingly, if defense requirements continue or increase, there will be a need for increased production capacity within the next five years.

Lithium developments were advanced by the demands of modern warfare. World War I saw the start of commercial development. World War II offered a much wider horizon, and in the past decade there have been startling developments in application. Up to this time, lithium products had been used in fields where the unique properties of lithium made it interesting in spite of its relatively high cost. In most present applications, lithium metal or lithium compounds are used in minor quantities in the manufacture of other products. Here again, the cost of lithium materials is not a major factor.

Sooner or later it must be recognized that other possible fields of application do not fall in these stated categories. Then lithium must compete with other materials in cost and in such cases quantity requirements will be large as compared with present consumption.

Lithium metal

Although this discussion is concerned chiefly with the growing demand for the element lithium, some reference should be made to the growth of lithium metal consumption, given in Table IV.

Lithium metal is used in a variety of industries, e.g., synthetic vitamins, antihistamines, and organic syntheses including promising application in rubber and petrochemical processes.

In metallurgy, lithium metal is used as a scavenger and degasifier, particularly in the nonferrous field. Considerable work has been done in the field of light metals, particularly lithium-magnesium alloy of high strength and low density. Alloys containing lithium are finding excellent use in brazing operations, and lithium metal has more than likely possibilities in the improvement of alloy and specialty steels.

Review of recovery process

It is not the purpose of this article to go into various ramifications of the winning of lithium, but a few significant factors become a part of the thesis of the lithium industry's growth.

The critical problem is extraction of lithium from its ores. The conventional processes are the sulfuric acid method and the lime method. Both require high temperature for decrepitation and subsequent leaching and purification, producing lithium carbonate as the end product in the acid method and lithium hydroxide in the lime method. The acid method is applied to low grade ores or concentrates and the lime method to concentrates. The lime method is better suited to the treatment of lepidolite (American Lithium Corp.). In any event the net recovery of lithium products is metallurgically very disappointing:

Acid method:	1 to 1.5 pct Li_2O	65 pct
	4 pct Li_2O	80 pct
	5 to 6 pct Li_2O	90 pct
Lime method:	5 to 6 pct Li_2O (spodumene)	
	3 to 3.5 pct Li_2O (lepidolite)	70 pct or better

If the losses in ore concentrating operations are included, then the recoveries from mine to finished product would appear to be as follows:

Acid method:	1 to 1.5 pct Li_2O	65 pct
	4 pct Li_2O	60 pct
	5 to 6 pct Li_2O	65 pct
Lime method:	5 to 6 pct Li_2O	50 pct or better

To reduce costs, therefore, any approach to process improvement must call for a means of increasing the amount of lithium extracted. At the same time, the simplification of plant design and reduction of investment in plant must also be weighed. There must be continued and extended research on recovery methods, as well as product research for new uses.

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Table I. Growth of the Lithium Industry in the U. S.

Year	Li_2CO_3 (or Equivalent), Lb
1935 through 1939 (average)	290,000
1940	370,000
1941	680,000
1942	980,000
1943	1,520,000
1944	2,780,000
1945	960,000
1946	1,060,000
1947	650,000
1948	960,000
1949	1,560,000
1950	2,430,000
1951	3,020,000
1952	4,160,000
1953	5,860,000
1954	9,660,000
1955	15,000,000
1956	Over 30,000,000

These figures up to 1955 were published by the U. S. Bureau of Mines. They represent the amount of lithium carbonate equivalent in the raw material mined, applying a factor of 66 pct recovery of finished product. While the fact is not shown, many of the earlier figures may not be accurate, as some mined material has been used directly, e.g., lepidolite or petalite in special glass manufacture.

Table II. U. S. Production Capacity of Lithium Carbonate or Its Equivalent in Thousands of Pounds Annually

Company	1946	July 1952	September 1954	1955	1956
Maywood Chemical Works	1,000	1,000	1,300	1,300	1,500
Lithium Corp. of America Inc.	3,000	3,000	3,000*	13,000	21,000†
Foote Mineral Co.	0	725	6,000	12,000**	12,000
American Potash & Chemical Corp. (inc. American Lithium Corp.)	0	1,175	1,500	1,700	7,700‡
Total—U.S.A.		5,900	11,800	28,000	42,200

* Prior to operation of plant at Bessemer City, N. C.
** Appears to be in excess of quantities of ore mined at Kings Mountain, N. C., and used in chemical plant at Sunbright, Va.
† Reflects potential capacity at Bessemer City, using concentrates instead of low grade ore.
‡ This figure includes data for plant at San Antonio, Tex. Earlier figures represent recoveries from brine recovery at Trona, Calif. The total figure is estimated and may be more or less as determined in actual full-scale operations.

Table III. U. S. Consumption of Lithium Carbonate or Its Equivalent

Use	(Li_2CO_3, in Thousands of Pounds) 1951, Estimated*	Pct	1955, Estimated**	Pct	1956, Estimated	Pct
Lubricating greases	816	27	3300	39	3500	11
Ceramics	779	26	1600	19	5000	15.7
Aluminum welding and brazing	287	9	1100	13	1520	4.7
Air conditioning	320	11	1100	13	1100	3.4
Batteries, primary and secondary	393	13	610	7	600	1.9
Pharmaceuticals	33	1	30	—	250	0.7
Metallurgical	not given		not given	—	30	0.1
Defense and miscellaneous	393	13	760	9	over 20,000	62.5
	3021	100	8500	100	00	100.0

* *Chemical Week*, Nov. 8, 1952 (Year 1951).
** Actual figures for the year 1955 for industrial consumption are probably more than 9 million lb total lithium carbonate or its equivalent. Actual figures are not available. The difference is allocated to "defense and miscellaneous."

Table IV. Consumption of Lithium Metal

Year	Pounds Per Year
Prior to 1914	Experimental lots for research
World production, 1914 to 1942	Less than 5,000
U. S., 1942 to 1946	Less than 100,000
U. S., 1947 to 1952	Less than 30,000
U. S., 1955, estimated	More than 100,000
U. S., 1956, estimated	More than 200,000
U. S., 1957, estimated	More than 300,000
Potential demand	1,000,000 ±

Diffusion of Calcium and Silicon in a Lime-Alumina-Silica Slag

Two additional experimental methods have been investigated for radioactive tracer studies of diffusion in liquid slags. Using the capillary method the diffusion constants of calcium and silicon at 1430°C are 1 x 10^{-6} and 1 x 10^{-7} $cm^2 sec^{-1}$ in a slag of 39 pct CaO, 40 pct SiO_2, 21 pct Al_2O_3. Heats of activation are approximately 70 kcal.

by Helen Towers and John Chipman

DEVELOPMENT of a simple radioactive tracer technique for measurement of the diffusion coefficient of calcium ion in liquid slag has already been reported.[1] The investigation was of a preliminary nature designed to explore the possibilities of using radioactive isotopes and to establish a method, and no great accuracy was claimed for the results. It was shown, however, that Ca^{45} could be used successfully, and the values obtained for the diffusion coefficient appeared to be of the right order of magnitude. However, it was considered that a better technique could be devised for carrying out the diffusion. The experiments were, therefore, continued to find a more accurate method, to check the calcium results, and to extend the investigation to include measurements of the diffusion coefficient of silicon in the same slag.

There were two flaws in the original technique. Convection was the cause of too many failures, and the interface between the two slags in the diffusion cell was curved rather than plane, probably due to a surface tension effect caused by the addition of the tracer Ca^{45} in the form of chloride. Two methods of overcoming these defects were tried. Since it was planned to study diffusion of the short-lived isotope Si^{31} also, the development of methods was restricted to those which gave promise of being reasonably rapid.

Method 1—The principle was identical to that previously used with respect to the diffusion conditions, but there were three differences in technique. Temperature control was more rigid, the tracer was added to the slag as $Ca^{45}O$ rather than the chloride and, finally, an effort was made to translate to high temperatures the elegant method developed by Cohen and Bruin[2] for bringing together the two liquid layers and beginning the diffusion.

A master slag was melted in graphite, ground to a fine powder, and analyzed (38.5 pct CaO-20.9 pct Al_2O_3-40.5 pct SiO_2). The tracer was received as $Ca^{45}Cl_2$ in an aqueous solution of $CaCl_2$ + HCl. From this, calcium oxalate was precipitated, ignited to calcium oxide, and added as such to the slag to give an activity of approximately 5 μc per g. The mixture was then melted into the form of a cylinder 3/16 in. diam and about 1 in. long. A solution identical to the tracer solution without Ca^{45} was given exactly the same treatment. The resulting $Ca^{45}O$ was mixed with that slag which was to form the tracer-free half of the diffusion cell, and this was likewise melted into a cylinder of the same size.

Slag cylinders, two with and two without Ca^{45}, were set in graphite blocks as shown in Fig. 1, and the crucible was lowered into position in the fur-

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TP 4441CE. Manuscript, Dec. 27, 1955. New York Meeting, February 1956.

The Transactions papers appearing in JOURNAL OF METALS *during 1957 will subsequently appear in AIME Transactions Volume 209, and may be permanently referenced to that volume.*

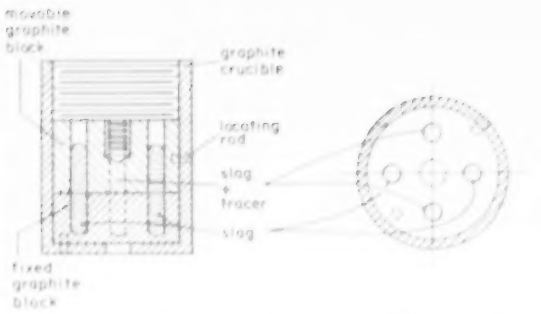

Fig. 1—Rotating block method for preparing diffusion couple.

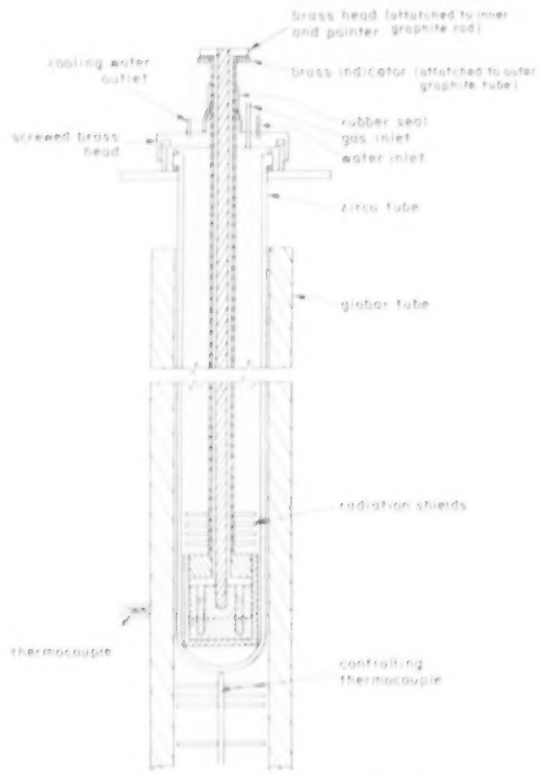

Fig. 2—Furnace assembly for diffusion studies.

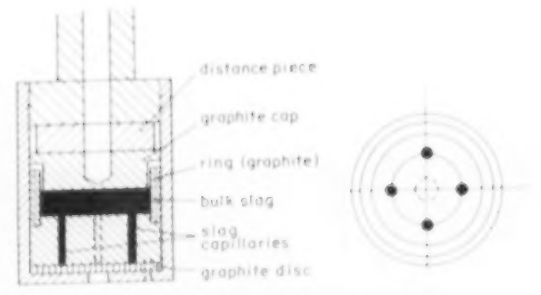

Fig. 3—Capillary method for diffusion in slag.

nace, Fig. 2. Temperature was measured by two Pt—10 pct Rh-Pt thermocouples, one outside the globar tube and the other, the controlling couple, immediately below the Zirco tube. The relationship between the temperatures recorded by these couples and that within the diffusion cell was found by an exploring couple and was frequently checked. When the diffusion assembly and the furnace had reached thermal equilibrium, the upper block was rotated through 90°, the correct position being fixed by the graphite locating pin moving in the crucible slot and checked by the brass guides at the upper ends of the graphite cylinders outside the furnace. Four diffusion cells were thus created simultaneously. Diffusion was ended by the cell being withdrawn rapidly from the furnace. The Ca^{45} concentration along each composite cylinder was measured and the diffusion coefficient calculated exactly as described previously.

Unfortunately, no greater precision was obtained by this method. The results generally confirmed those previously determined but retained the same scatter. Much of the difficulty once more concerned the interface. As the liquid was being sheared during rotation, each half became free to adopt a new and more nearly equilibrium shape with respect to the graphite. Since the contact angle of this slag on graphite is about 160°, all the sheared surfaces were convex instead of plane. When two such surfaces were brought into contact to create the diffusion cell, it was impossible for a plane interface to result. This problem is not incapable of solution. The slag could be made to have a contact angle of $<90°$ either by reaction with the graphite or by a minute addition of a surface-active component, but either method might well create new problems. Alternatively, the slags could be placed under restraint by having them totally enclosed in graphite and allowing no freedom of movement. In the meantime, however, trials were being made with a second method which showed more immediate prospect of success.

Method 2—This was based on the capillary principle. Slag capillaries to which tracer had been added were brought into contact with a relatively large volume of the master slag. After diffusion, the concentration of tracer along the capillary was measured and, from this, the diffusion coefficient could be calculated.

The capillaries containing $Ca^{45}O$ were 1/16 in. diam and ½ in. long. Four such capillary rods polished on each end were inserted into closely fitting capillary tubes in a graphite block. The master slag was melted into the shape of a disk, one face of which was then polished. This was held inside a graphite ring on top of the block containing the capillaries, as shown in Fig. 3. The usual $Ca^{45}O$ addition to compensate for the amount of tracer in the capillaries was not made since it was considered that there would be less tendency for disturbance if the capillaries were slightly denser than the bulk slag. A graphite plug fitted into the ring above the slag disk and pressure applied to this plug prevented any movement. This was found to be necessary since the surface tension of the slag was high enough to withdraw the slag completely from the capillaries in the lower block.

The same general assembly as in Fig. 2 was used to contain the diffusion cell. This was lowered rapidly into the furnace, which was maintained at the desired temperature. Thus, the exact time for the beginning of diffusion was not known. To minimize convection, the cell was placed slightly below

the plane of highest temperature, making the temperature at the top of the cell about 0.5° above that at the bottom. At the end of diffusion, the cell was withdrawn as quickly as possible and allowed to cool in air. The capillaries were detached from the slag disk, mounted, polished, and autoradiographed. A microphotometer trace was made in each case, the general appearance being very similar to that reported in the earlier paper.[1] Typical capillaries and a trace are shown in Fig. 4.

Calculation of the Diffusion Coefficient D—If the concentration at the capillary exit is equal to zero at all times, the concentration distribution within the capillary is a function of time and distance x from the capillary exit. A solution of the analogous heat flow problem, the case of a semi-infinite solid initially at constant temperature with zero temperature in the plane $x = 0$, is available. The corresponding equation for mass transfer is

$$f(x,t) = \frac{C(x,t)}{C_s} = \text{erf}\,\frac{x}{2\sqrt{Dt}} \qquad [1]$$

where $C(x,t)$ is the concentration of diffusing substance in capillary at time t and distance x from the exit plane, and C_s is the initial concentration in capillary. This equation has often been used to evaluate the results of measurements with capillary diffusion cells and is a good approximation for long times when the concentration at the exit is maintained at a low level by rapid stirring of the bulk liquid.

In the present case, the concentration at the end of the capillary is finite since convection in the bulk was avoided, and hence there is a finite resistance to mass transfer between the exit plane of the capillary and the bulk slag outside the capillary. However, conditions in the exit plane will vary with the distance from the center of the capillary. For an approximation, an average value of the mass transfer coefficient k may be introduced. The solution of the analogous heat flow problem, that of the semi-infinite solid, initially at constant temperature, radiating into a medium at zero temperature, has been given by Carslaw and Jaeger.[7] The corresponding equation for mass flow is

$$g(x,t) = \frac{C(x,t)}{C_s} = \text{erf}\,\frac{x}{2\sqrt{Dt}} + \exp\left(\frac{kx}{D} + \frac{k^2t}{D}\right)\text{erfc}\left(\frac{x}{2\sqrt{Dt}} + k\sqrt{\frac{t}{D}}\right) \qquad [2]$$

For ease of evaluation the equation was written

$$g(x,t) = \frac{C(x,t)}{C_s} = \text{erf}\,\frac{x}{2\sqrt{Dt}} + \exp\left(-\frac{x^2}{4Dt}\right)\exp\beta^2\,\text{erfc}\,\beta \qquad [3]$$

where $\beta = \dfrac{x}{2\sqrt{Dt}} + k\sqrt{\dfrac{t}{D}}$. For $\beta < 3$, values of $\exp\beta^2\,\text{erfc}\,\beta$ have been tabulated; while for $\beta > 3$, the function was evaluated from a series expansion.

The experimental results for $\dfrac{C(x,t)}{C_s}$ may be plotted on rectangular coordinates and compared with theoretical curves obtained by inserting values of D and β in Eq. 3. It is difficult to obtain a fit by this method because of the curvature of such a plot, especially for small values of x. The exact location of the exit plane of the capillary could not always be determined since the slags fractured irregularly in disassembling the cell. The experimental results are therefore expected to be least accurate near the capillary exit, where x is small.

A better method was found in plotting the results on arithmetical probability paper. The nonlinear ordinate on such paper is scaled from 0.01 to 99.99 according to the cumulative Gaussian distribution and is thus symmetrical about scale number 50. It is therefore possible to plot functions such as $50(1 + \text{erf}\,z)$ as straight lines through ordinate scale number 50. Thus $f(x,t)$ in Eq. 1 may be *rectified* to plot as a straight line on such paper. Similarly, $g(x,t)$ in Eq. 2 is also found to give a straight line, at least for values of $k\sqrt{\dfrac{t}{D}} > 0.5$, essentially parallel to that for $f(x,t)$. The ordinate intercept

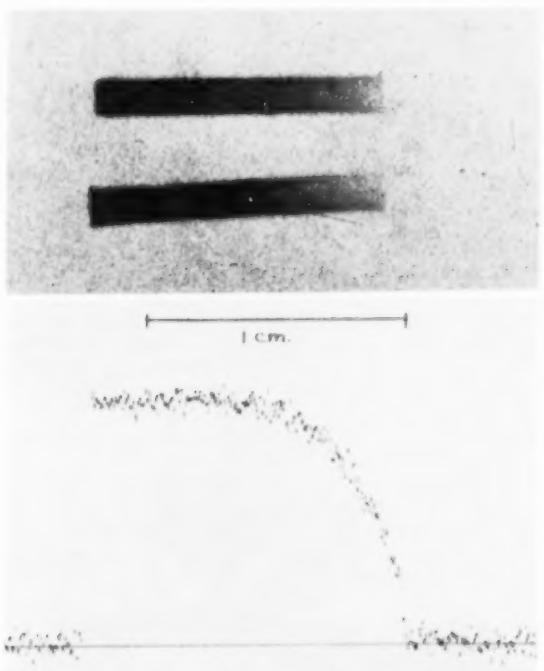

Fig. 4—Autoradiograph and microphotometer trace of diffused slag cylinders. X6. Reduced approximately 40 pct for reproduction.

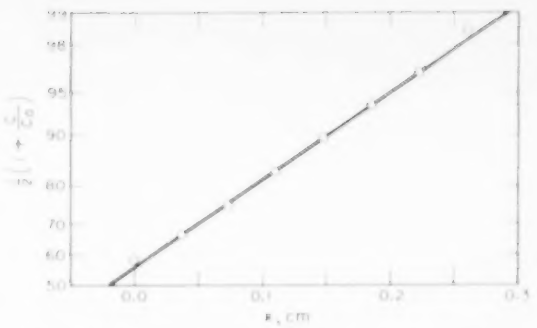

Fig. 5—Typical plot of experimental results on arithmetical probability coordinates.

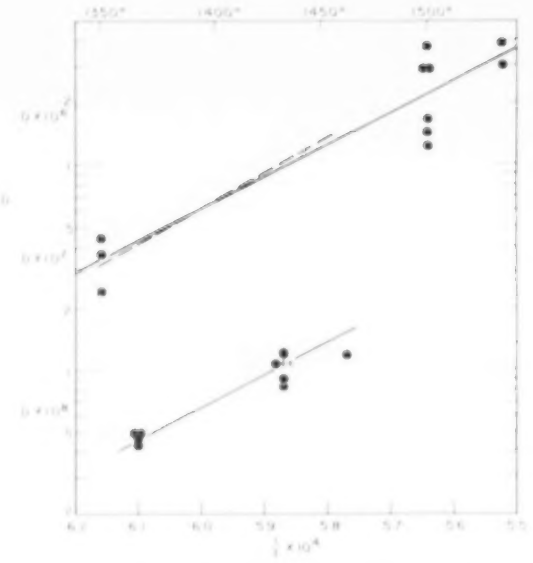

Fig. 6—Diffusion coefficients of calcium (upper line) and silicon (lower line). Broken line shows earlier results for calcium.

is, however, greater than 50 and depends on the value of $k\sqrt{\frac{t}{D}}$.

Accordingly, the experimental results were plotted on probability paper, using ordinate values of 50 $\left(1 + \frac{C(x,t)}{C_s}\right)$. The typical plot shown in Fig. 5 deviates slightly from a straight line for small values of x. From the slope of the linear portion the value of D could be readily evaluated.

The results are shown in Fig. 6, where log D is plotted against $\frac{1}{T}$. Measurements were made at three temperatures selected at the limits of the available temperature range. Average values of D at 1350°, 1500°, and 1540°C, respectively, are 3.5×10^{-7}, 2.1×10^{-6}, and 3.4×10^{-6} cm² sec⁻¹. The results of the previous study are given for comparison on the same graph. The slope of the line corresponds to 70 kcal for the energy of activation.

Diffusion of Silicon—The isotope Si^{31} emits β rays of maximum energy 1.8 mev and has a half-life of about 2.7 hr. Measurement of silicon diffusion in liquid slag thus presented a twofold difficulty: a) a short half-life coupled with an expected low value of D, and b) a high intensity of radiation in relation to the low density of the slag. It was realized in advance that autoradiography was scarcely the ideal method of measurement of concentration, but the short half-life rendered a quick method necessary and ruled out the possibility of, for example, a grinding technique whereby aliquot layers could be counted for activity. Method 2 described above was, therefore, used with the modification that in some experiments the tracer was contained in the bulk slag. Since addition of SiO_2 decreased the density, the tracer-free slag was located in the lower section of the cell.

Si^{31} was obtained by deuteron bombardment of finely ground high-purity silicon in the Massachusetts Institute of Technology cyclotron. The silicon was obtained through the courtesy of the duPont Co. and contained less than 10 ppm total impurities, of which 2 to 5 ppm were iron, with copper less than 1 ppm. The silicon powder, activity 8 mc per g, was then oxidized to SiO_2 by treatment with sodium hydroxide, hydrogen peroxide, and perchloric acid. The SiO_2, weighing about 0.12 g, was mixed into 6 g of the finely powdered master slag and the mixture melted, stirred, and made into the form of a disk in the manner already described. Capillary rods, 1/16 in. diam, were withdrawn during the melting process to be used as standards in the ultimate photography and to provide the reference value of C_s. The procedure for carrying out the diffusion was the same as before. As the diffusion went on, the decrease in activity of the standards was checked with a G-M counter. This confirmed the purity of the radiation and enabled the maximum diffusion time to be given consistent with obtaining a photographic record. With the specific activity quoted above, the maximum time allowable between making the Si^{31} and the beginning of the photographic exposure was found to be about 24 hr. The first 3 hr of this was lost because the target holder was too *hot* to be handled. It was possible to do several runs from a single Si^{31} sample, in one case three runs of 3, 5, and 10 hr being carried out at different temperatures. The longest time given for diffusion in any one run was 15 hr; in general, times between 5 and 10 hr were normal.

Correction for High Penetration Range—The high intensity of the β radiation coupled with low slag density did not make for high resolution in the photograph. The short diffusion distance accentuated the disadvantage. For the autoradiographic method, it is usually considered that the energy of the rays should be so low that their range of penetration is an order of magnitude less than the diffusion distance. In the case of Si^{31}, the range R is about 0.25 cm (calculated from $R = \frac{0.546\,E_m - 0.16}{\rho}$, where E_m = maximum energy of the β rays in mev, and ρ = density of the medium in g cm⁻³); this is of the same order as the diffusion distance. The autoradiographs could only be described as fuzzy, and the exact diffusion coefficient is correspondingly uncertain.

The true value of $C(x,t)$ is not obtained directly from the photographic record of C vs x at time t, and can only be found by taking into account the radiation from layers behind the surface and integrating over the diffusion length. The labor involved in the strictly mathematical solution for this correction seems altogether unwarranted. A practical solution was obtained in the following manner. Two capillary rods, one with and the other without tracer addition were joined end to end, and an autoradiograph was made of the longitudinal section. Across the junction no diffusion had taken place and, had the range of β penetration been sufficiently small, the microphotometer trace would have approached the form shown in Curve I of Fig. 7. In fact, it resulted in a graph such as Curve II, and this was used for correcting the experimental curves. The line AB denotes the junction between the two capillaries. The intensity at each point along YM results from radiation not only at that point but from points in all directions extending as far as the limit of β penetration. The observable limit of β

penetration is the distance BZ. Along the length YA the intensity XY is less because no radiation is being received from points beyond A. Similarly, the recorded intensity XZ is due to radiation received from AY. The area under XZ was accordingly treated as proportional to the amount of extraneous radiation and was subdivided lengthwise into units. Similarly, the area XAY was divided into units of length and the radiation deficiency in each unit was obtained. Correction factors were derived for the fractional excess or deficiency of radiation received by each unit of distance, and these were applied to the experimental curves. Corrected graphs were then drawn as in Fig. 8, from which D values were calculated in the usual manner.

The arithmetical method of correction is about equivalent to the first approximation which would be obtained by integration. However, it was found that a) applying the arithmetic correction factors a second time, and b) multiplying the number and thereby decreasing the size of the steps both had negligible effect on the correction. While a mathematical solution of the problem based on the fundamental data of β-ray penetration would be more elegant, it is doubtful if it would be more accurate, largely because it is difficult to see how account could be taken of the *Bremsstrahlung* effect.

Results

Diffusion runs were made at 1365°, 1430°, and 1460°C. Average values of D at 1365° and 1430°C are 4.7×10^{-8} and 1.05×10^{-7} cm²sec⁻¹. The results are shown in Fig. 6, where log D is plotted against $\frac{1}{T}$. Of the seven points at 1430°C, four were obtained with tracer originally in the bulk slag, and three with tracer originally in the capillaries. In each case the active, lower density slag was placed on top. Only one result was obtained at 1460°C, and

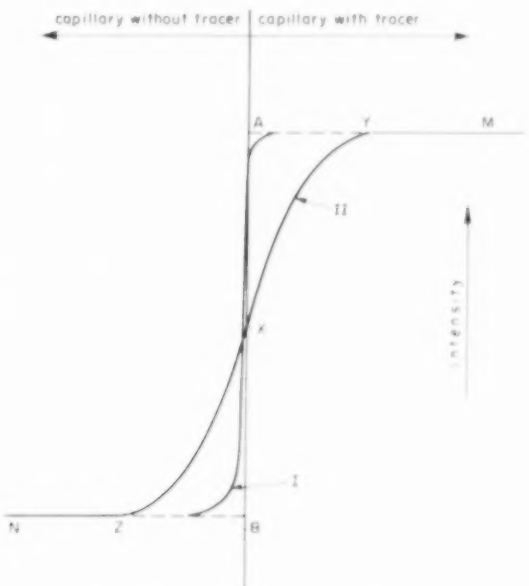

Fig. 7—Schematic diagram of radiation intensity at plane interface before diffusion. Curve I for Ca^{45}, 0.2 mev; Curve II for Si^{31}, 1.8 mev.

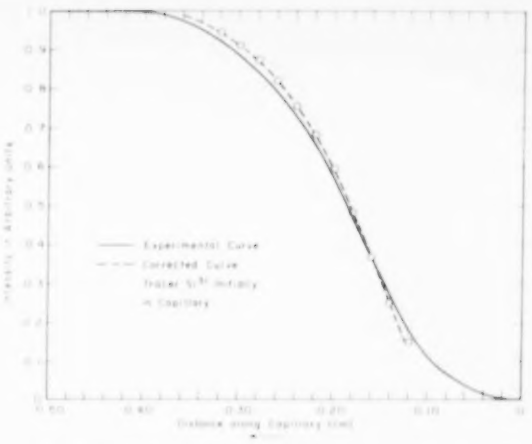

Fig. 8—Diffusion curve for Si^{31}, showing correction for high penetration.

this value is therefore unsupported. The tentative line indicates an activation energy of roughly the same magnitude as found for calcium.

Discussion

In the case of the calcium measurements the diffusing unit has been assumed to be calcium ion Ca^{++}, and it has been shown[1] that the experimental values of D agree approximately with conclusions which might be reached from conductance measurements. The much higher activation energy for diffusion than for conduction, however, indicates the possibility of a diffusion mechanism more complex than simple ionic movement.

The results for silicon give little information about the mechanism of the silicon diffusion process. Comparison with the allied processes of electrical conduction and transference would appear to eliminate certain possibilities. The value of D_{Si} is about one tenth that of D_{Ca}. If the diffusion were that of an ion of charge 2 or 4, the ion should have a transport number of about 0.1 or 0.2, which seems precluded by the results of Bockris and co-workers.[4] The diffusion of silicon would, therefore, appear to be something other than simple ionic movement. A mechanism involving the rupture of two of the bonds by which an SiO_4 tetrahedron is held to the silicate network or to a large ion would permit movement of two oxygens along with the silicon, resulting in no net transfer of charge.

Further studies of diffusion of Ca^{45}, Si^{31}, and O^{18} in slags of a range of compositions would contribute valuable information for the study of slag structure.

Acknowledgments

Grateful acknowledgment is made to the American Iron and Steel Institute for its support of this research. The authors wish to thank C. Wagner, T. B. King, and T. Forland for helpful discussions.

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Some Notes On Oroya Copper Slags

This paper is a study of the interrelationship between copper and magnetite content of reverberatory slags. During an experimental run converter slag was withheld from a reverberatory, resulting in much cleaner waste slags. The possibilities of treating converter slags outside the normal copper smelting circuit are briefly discussed.

by I. L. Barker, J. S. Jacobi, and B. H. Wadia

ALTHOUGH valuable information has been published on the important problems of slag losses with which every copper metallurgist has to contend, a great deal of money is still being wasted in copper smelters all over the world, through metal being *irretrievably* lost in reverberatory slags. When smelting a relatively low-grade pyritic concentrate together with a proportion of direct-smelting oxidized ore, as is done in Oroya, slag volumes are of necessity high, and even a relatively *clean* slag, say of 0.5 pct Cu, means a loss of almost 4 pct of all the copper charged, or over $1,000,000 annually at present output and prices.

While it is known that such losses can often be reduced by allowing the slag time to settle, with or without addition of a reducing agent such as coal or pyrite, the facilities for such treatment are not always available in a plant of old design working to capacity under severe space limitations.

Nor is it easy under such conditions to run large scale tests which may endanger the smooth flow of production for considerable periods without yielding

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TP 4433D. Manuscript, Feb. 22, 1956. New York Meeting, February 1956.

At the left is an aerial view of the La Oroya metallurgical works of the Cerro de Pasco Corporation. The plant is located at an altitude of 12,200 ft, 120 miles northeast of Lima, Peru.

positive results. It was, however, possible to run the 24 hr full scale test described, to see what would happen if the converter slag was kept out of the smelting circuit altogether. The results indicate that, apart from reducing the slag volume, the copper content of the slag is also considerably cut and the total losses are cut by 3.27 tpd or 2.2 pct of the total copper charged to the reverberatories. This calculation includes a prospective loss in treating the converter slag separately by leaching, in which preliminary results indicate that 93 pct recovery of the copper in converter slag could be obtained.

The economics of treating the converter slag by a separate process will depend on a) the copper price, b) the scale and cost of operations, and c) how far the increased reverberatory capacity and furnace life, which undoubtedly would result from keeping the converter slag out of the system, could be utilized for increased copper production.

Table I. Average Specific Gravity of Reverberatory Slags*

Slag As Cast	Cast Slag Broken Into ¾ In. Pieces	Cast Slag Ground to —100 Mesh
3.58	3.66	3.86

* The above average values are taken from ten different samples, each of which showed approximately the same relative relationship.

In Oroya the problem would involve putting up a separate milling and leaching plant for 500 tpd converter slag containing an average 2.5 pct Cu. Technically, there appear to be good possibilities with either sulfuric acid-ferric sulfate leach or the ammonia leach under pressure.

General Description

The Oroya copper reverberatories, on the slags of which most of the data presented in this paper have been gathered, are situated in the Peruvian Andes at an altitude of 12,200 ft. The furnaces are of conventional design, about 100 ft in length and 25 ft across. Charging is done along the side-walls, hot calcine being brought to the top of the furnaces from the roasters by trolley cars. Slag skimming is done at one end while the matte may be tapped from either side of the furnaces. The slag temperature averages about 1215°C, with the matte temperature about 180°C lower.

To observe the effect of settling and of addition agents on the reverberatory slags, an oil-fired tilting furnace holding a No. 35 Salamander crucible (approximately 25 lb slag capacity) was set up near the slag skimming door. Crucibles of different materials were tried, but the Plumbago type was finally selected for the test work in spite of its drawbacks. This type of crucible is mechanically strong and will resist corrosion by the slag for several hours, but unfortunately it is not inert chemically and has a reducing effect on the slag. Crucibles made of acid material are still less desirable, and a basic crucible which is cheap, inert, and sufficiently heat resisting has not yet been found. An attempt is now being made to apply a wash of high alumina cement to the inside of the Plumbago pot, which should prevent direct contact of the slag with graphite. Samples of molten reverberatory slag were taken during skimming and ladled from the stream directly into the crucible furnace, which was already at the slag temperature. The experiments were carried out in this furnace, the temperature of which was held constant throughout.

Fig. 1—Micrograph of reverberatory slag shows massive and dendritic magnetite and rounded particles of copper sulfide. X600. Reduced approximately 25 pct for reproduction.

Table II. Average Composition of Cast and Granulated Slags*

	Specific Gravity, —100 Mesh	Magnetite	Total Copper
Cast	3.71	7.2	0.33
Granulated	3.46	5.9	0.32

* The above average values are taken from eight pairs of samples, each of which showed approximately the same relative relationship.

Sampling

In order to ascertain whether the means of sampling would cause significant differences in analysis, the following points were investigated: 1) the effect of particle size of the sample on specific gravity, and 2) the differences in specific gravity and magnetite content between chilled and slowly cooled slags.

It was first established by experiments that it is sufficient to grind the slag samples for analysis to —100 mesh to obtain consistent results. Unless other-

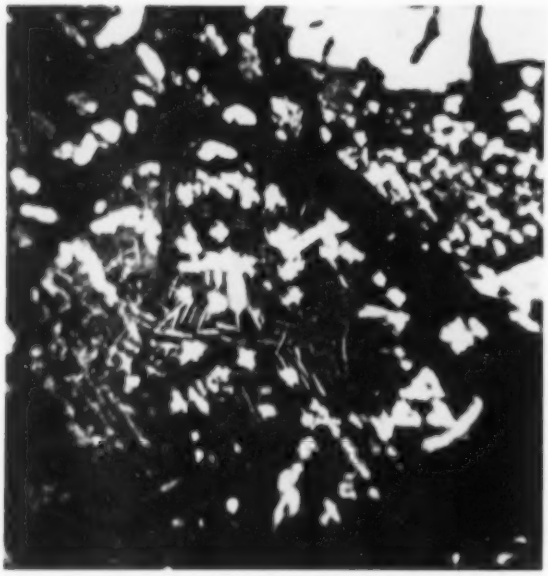

Fig. 2—Micrograph of reverberatory slag shows grayish needles of delafossite. X600. Reduced approximately 30 pct for reproduction.

wise stated, therefore, all analyses in this paper are on granulated samples ground to that fineness.

As cast slags are broken up into smaller pieces, there is a distinct increase in specific gravity, as shown in Table I. This is of course due to porosity in the cast slag and is evidence of non-equilibrium conditions in the slag leaving the furnace. To show the effect of different cooling rates on specific gravity and magnetite content, a number of samples were divided by casting one portion into a fireclay crucible, which was allowed to cool very slowly, while the other portion was poured into water and granulated. Table II shows a consistent difference in specific gravity and magnetite of cast and chilled slags, while the total copper content remains the same.

One of the authors had done work along similar lines some years ago, and these results are presented in Table III. The composites of both *cast* and *granulated* samples of Table III were remelted and again subdivided into slowly cooled and chilled samples, as indicated. The effect of cooling rates on magnetite content is very striking and has been confirmed by more recent work by the present authors. However, the results are not strictly comparable because of different and, it is believed, more reliable methods of magnetite analysis which have since been developed. Although quantitatively the earlier work cannot be supported, it nevertheless appears valuable as indicating the general tendency of magnetite formation, and as the basis for the further work now being carried out.

Table III. Earlier Work on Cast and Granulated Slags

	Specific Gravity, 100 Mesh	Total Iron	Magnetite, Fe_3O_4
Average*			
Cast	3.93	40.5	8.8
Granulated	3.58	39.2	2.1
Original			
Cast	3.93	39.6	7.6
Granulated	3.58	39.1	0.6
Remelts			
Cast-Cast	3.93	39.8	2.4
Cast-Granulated	3.68	39.6	0.3
Granulated-Cast	3.81	38.9	3.1
Granulated-Granulated	3.63	38.7	0.3

* The above average values are taken from seven pairs of samples, each of which showed approximately the same relative relationship.

One very important variable which has not so far been studied, but which the authors hope to examine in the near future, is the temperature from which the slags are quenched. Obviously, as magnetite is the first solid constituent to crystallize out from the molten slag magma, it has a very important bearing on the subject. All the work reported in Table II was done at temperatures of $1220° \pm 15°C$ as checked frequently by the optical pyrometer.

The question then arises as to what the correct values are for the items under discussion when the slag is in the furnace in the molten state, as it is of greatest importance to the metallurgist when in this condition. Although it is difficult to determine the exact ionic nature of the molten slag, it seems justifiable to assume that the conditions found in granulated or rapidly chilled samples are fairly close to those prevailing in the molten state. The rapid change from the liquid to the solid state would allow little time for rearrangement or alteration of crystalline structure or for any interaction to take place.

Methods of Analysis

Total copper was analyzed by the usual iodide method.

Analyses of *non-sulfide copper* were made according to the sulfurous acid method of Van Barneveld and Leaver. It is claimed that this method differentiates between copper sulfides and all other forms of copper, including metallic. For ores, at least, this is true. Whether it is equally applicable to slags and other such products is somewhat uncertain, but it is still the best method yet developed for the purpose.

The method used for magnetite determination[1] is based on the addition of an accurately measured amount of stannous chloride to the sample, after which the sample is decomposed with HCl and HF. The excess stannous chloride is titrated with a

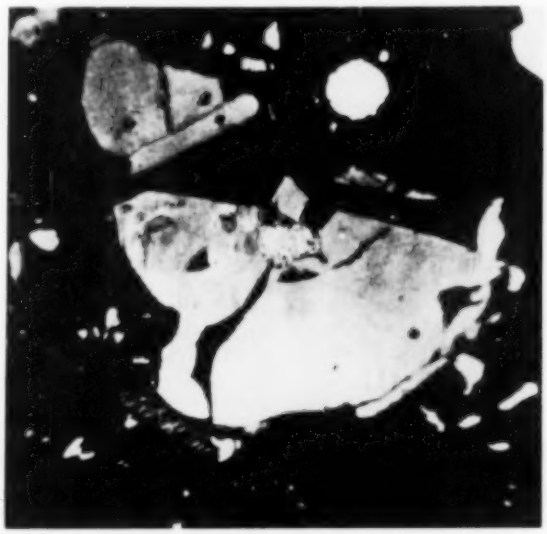

Fig. 3—Micrograph of reverberatory slag shows metallic copper particle locked in massive magnetite. X600. Reduced approximately 30 pct for reproduction.

Table IV. Settling and Modifying Tests on Reverberatory Slags*

Type of Test	Sampling Time, Min	Cu, Pct	Magnetite, Pct	Total Fe, Pct	SiO_2, Pct	CuO, Pct
Settling test on normal furnace charge smelted in crucible	0	10.8	3.0	32.0	22.8	0.01
	30	9.86	2.4	30.1	25.8	Trace
	60	8.29	1.4	28.0	29.2	Trace
	90	8.70	1.5	27.7	28.6	Trace
	120	7.53	0.5	27.2	30.6	Trace
	150	3.32	0.7	23.4	42.6	Trace
	180	1.64	0.6	23.9	40.2	Trace
	210	0.22	0.5	21.6	45.0	Trace
	210†	15.6	1.0	30.1	11.8	Trace
	210‡	20.9	4.4	32.0	1.2	0.01
Settling test on molten reverberatory slag	0	0.57	6.3	32.7	36.5	0.04
	30	0.34	3.9	34.8	34.5	0.01
	60	0.38	2.1	34.3	36.0	Trace
	90	0.28	0.1	35.0	36.6	0.01
	120	0.20	0.4	34.3	37.8	0.01
Molten reverberatory slag with pyrite additions	0	0.32	9.0	35.1	33.9	0.01
	30	0.25	6.2	32.6	37.3	0.01
	60	0.15	4.3	30.1	34.9	Trace
	90	0.06	0.1	28.3	36.6	Trace
	120	0.09	2.5	33.0	34.7	Trace
	150	0.09	0.7	31.8	36.6	Trace
	180	0.06	0.1	32.7	37.4	Trace
	180‡	0.91	0.1	45.8	25.3	Trace
Molten reverberatory slag with silica additions	0	0.63	11.2	39.4	29.2	0.01
	30	0.94	5.7	37.9	31.0	Trace
	60	0.56	3.7	38.9	31.2	0.01
	90	0.71	1.0	38.7	31.4	0.01
	120	0.91	1.1	38.3	33.6	0.01
Molten reverberatory slag stirred with siliceous floating top layer	Sol. 0	0.66	7.5	33.2	37.0	0.10
	Liq. 0	0.39	4.9	31.4	37.0	0.02
	30	0.30	3.5	30.7	37.0	0.02
	60	0.18	0.3	30.3	39.3	0.02
	90	0.16	0.1	29.6	42.0	0.01
	120	0.13	0.1	29.1	42.4	0.02
	150	0.17	0.1	29.9	42.2	0.01
	150‡	0.54	0.1	31.0	39.6	Trace
Settling test on converter slag remelted from cold	0	0.87	9.8	49.4	22.2	0.05
	30	0.86	10.1	49.2	21.9	0.05
	60	0.86	10.1	49.0	22.4	0.08
	90	0.82	11.1	49.5	22.0	0.10
	120	0.82	10.6	39.8	21.5	0.10
	120‡	7.09	6.0	45.4	18.6	0.71
Settling test on converter slag remelted from cold with pyrite additions	0	1.75	9.4	47.1	19.6	0.01
	30	1.17	9.4	50.8	27.5	0.01
	60	1.05	0.1	46.0	29.2	Trace
	90	1.01	0.1	46.1	29.2	Trace
	120	0.77	0.1	50.2	19.2	Trace
	150	0.48	0.1	50.4	19.6	0.02
	150†	1.09	0.1	51.6	21.6	0.01
	150‡	1.39	0.1	48.8	24.4	Trace
Settling test on converter slag remelted from cold with silica additions	0	1.58	5.9	48.2	23.3	0.08
	30	0.93	7.8	46.1	25.8	0.08
	60	0.74	5.2	46.8	26.2	0.08
	90	0.75	4.5	47.1	27.4	0.06
	120	0.77	6.4	47.2	27.7	0.07
	150	0.76	7.0	47.0	27.7	0.11
	180	0.74	6.5	47.0	27.8	0.11

* All the above experiments were carried out in a crucible holding 25 lb of slag at 9 in. effective depth. All samples were taken 1 in. from the top except those footnoted below.
† Sample taken 5 in. from the top.
‡ Sample taken 1 in. from the bottom.

Table V. Special Reverberatory Test Run—Material Balance

Normal Operation (two furnaces), November 30, 1955*

		Assay, Pct					Distribution, Pct				
	D.S.T.	SiO_2	Fe	CaO	S	Cu	SiO_2	Fe	CaO	S	Cu
Materials In:											
Calcine	1510	19.8	30.3	4.7	18.5	9.90	76.5	65.3	89.1	97.5	92.8
Converter Slag	480	19.2	50.8	(1.8)	(1.5)	2.40	23.5	34.7	10.9	2.5	7.2
	1990						100.0	100.0	100.0	100.0	100.0
Materials Out:											
Matte	610		34.0		25.0	26.0		29.4		53.5	98.59
Reverb. Slag	1350	32.4	38.9	5.7		0.45	111.5	74.5	98.5		3.77
Cottrell Dust	31	6.8	5.8	1.6	2.7	4.36	0.5	0.2	0.6		0.83
Unaccounted for Loss (Gain)	(1)						(12.0)	(4.1)	2.9	46.5	(3.10)
	1990						100.0	100.0	100.0	100.0	100.00

The Above Recalculated for Conditions Established After 20 Hr Test Run Without Converter Slag.†

Materials In:											
Calcine	1510	19.8	30.3	4.7	18.5	9.90	100.0	100.0	100.0	100.0	100.0
Materials Out:											
Matte	610		34.0		25.0	26.0		45.5		55.0	106.06
Reverb. Slag	870	45.3	22.3	(7.0)	(1.0)	0.23	132.0	42.5	86.0	3.1	1.34
Cottrell Dust	31	6.8	5.8	1.6	2.7	4.36	0.7	0.4	0.7	0.3	0.90
Unaccounted for Loss (Gain)	(1)						(32.7)	11.6	13.3	41.6	(8.30)
							100.0	100.0	100.0	100.0	100.00

* Total copper lost in reverberatory slag is 6.68 tons in 24 hr.
† Total copper lost in reverberatory slag is 2.09 tons in 24 hr.

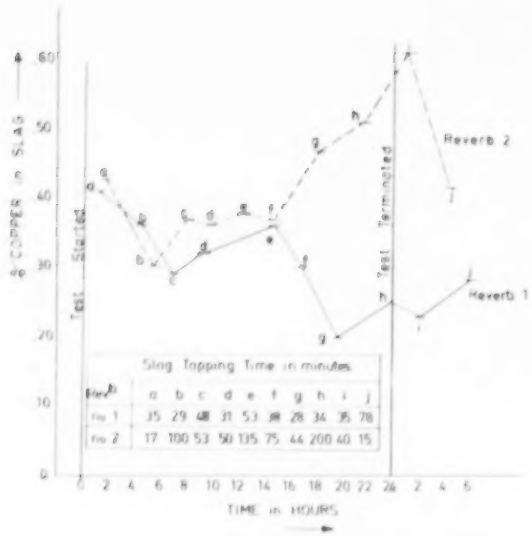
% COPPER in SLAG
Test Started
Test Terminated
Reverb 2
Reverb 1
Slag Tapping Time in minutes
Rev.
a b c d e f g h i j
no 1 35 29 48 31 53 38 28 34 35 78
no 2 17 100 53 50 135 75 44 200 40 15
TIME in HOURS

Fig. 4—Special 24 hr reverberatory run. Reverberatory No. 1 was without converter slag; reverberatory No. 2, with twice the usual amount of converter slag.

known strength of iodine solution. This method stood up best in comparison with other methods for magnetite analysis and gave very good results with known additions of standard magnetite obtained from the National Bureau of Standards. Even so, it seems also to include some of the Fe_3O_4 that may be present in the slag. Because of the difficulty of assaying magnetite by chemical methods, Cerro de Pasco Corp.'s petrologist is developing a method which uses the geophysical magnetometer. With standardization of sample distance, density, etc., the method shows good chances of success. Occasional small amounts of pyrrhotite, etc., are not large enough to interfere.

Table VI. Copper Balance

Total copper lost in reverberatory slag at present	6.08 tons per 24 hr
Total copper lost without returning converter slag to the circuit	2.00 tons per 24 hr
Gross saving	4.08 tons per 24 hr
Deduct copper lost in separate processing of converter slag, 7 pct at 480 tons per day containing 2.4 pct Cu	0.81 tons per 24 hr
Net saving in copper*	3.27 tons per 24 hr

* This is equivalent to 2.2 pct of the copper charged in our calcines.

Forms of Copper Found in Reverberatory Slags

Exact research work on reverberatory slags is almost impossible because of the many variables, such as charge and slag composition, general furnace conditions, slag temperatures, converter slag additions, cooling rates, etc. Therefore, copper metallurgists differ widely on the forms in which copper occurs in reverberatory slags.[2,3] Most recent investigators are of the opinion that a large percentage of the copper in these slags is present as sulfide inclusions. Similar evidence has been obtained in the present chemical analyses, leach tests, microscopic work, etc., which supports this assumption, see Fig. 1.

Microscopic polished section studies of Oroya copper slags were undertaken by the petrologist and have revealed the following to be usually present: silicates: fayalite, melilite, pyroxene; oxides: magnetite, spinel, delafossite, tenorite, cuprite; sulfides: pyrites, digenite, chalcopyrite, bornite, covellite; and metals: copper.

The presence of delafossite ($Cu_2O\ Fe_2O_3$), see Fig. 2, has been frequently noted in the reverberatory slags and seems to be related to the amount of oxide ore fed into the circuit. An appreciable portion of the copper minerals is mechanically locked in coarse magnetite, see Fig. 3. This confirms the general impression that copper loss is directly related to the magnetite content. Such a relation is also evident from Figs. 4 and 5. Although this relationship does not always show itself in individual random samples, Figs. 4 and 5, which were plotted from composites of no fewer than 197 samples taken during a 24 hr period, are fairly representative and prove the direct connection between copper losses and magnetite.

Settling and Modifying Tests on Reverberatory Slags

To obtain some pointers for future large-scale tests, experiments were carried out in the crucible furnace on settling of the molten slag and on addition of pyrites and silica. Attention was also directed to the mushy silica layer which can so often be observed floating on top of reverberatory slags, particularly when furnaces are hard driven. Each of these experiments was repeated at least three times. The results are summarized in Table IV.

As previously stated, a slight reaction takes place between the slag and the crucible wall. This, however, is limited to the periphery, the center portion of the slag lying undisturbed. Even this slight reaction apparently ceases when the magnetite content of the slag is reduced to a negligible amount.

The following trends were noticed in the results of these experiments:

1) Copper in the slag definitely settles to lower levels with time.

2) The addition of pyrites by sprinkling on top of the slag also lowers the copper content of the top layers. Copper removal appears to be faster and more complete than by gravity alone, which indicates that pyrite has a cleansing effect of its own although the mechanical sedimentation effect of copper may be preponderant.

Table VII. Slag Leaching by Sulfuric Acid, Followed by Ferric Sulfate

First Leach:* Temperature, 60°C; Time, 2 Hr				Second Leach:† Temperature, 60°C; Time, 6 Hr		Combined
	Pct of Extraction					
Slag Type	Cu	Fe	Zn	Slag Type	Extraction of Cu, Pct	Extraction of Cu, Pct
Reverb.	nil	73.5	80.0	Reverb.	91.5	91.5
Reverb.	nil	79.0	98.0	Reverb.	95.7	95.7
Reverb.	nil	72.0	85.0	Reverb.	93.1	93.1
Reverb.	nil	57.0	78.0	Reverb.	88.7	88.7
Reverb.	nil	69.0	79.0	Reverb.	89.3	89.3
Reverb.	nil	85.0	97.0	Reverb.	97.4	97.4
Reverb.	nil	76.0	87.0	Reverb.	94.8	94.8
Reverb.	nil	70.0	81.0	Reverb.	93.0	93.0
Average	0.0	72.7	85.6	Average	92.9	92.9
Conv.	27.5	66.4	83.7	Conv.	93.0	95.4
Conv.	30.2	64.5	84.5	Conv.	91.7	94.1
Conv.	30.6	67.2	85.5	Conv.	92.6	94.5
Conv.	29.3	65.0	85.0	Conv.	92.5	94.3
Average	29.4	65.8	84.7	Average	92.4	94.6

* 100 g slag, 1000 ml solution containing 90 g H_2SO_4.
† Filter residue 100 g from first leach with 1000 ml of solution containing 35 g H_2SO_4 and 1 g $Fe_2(SO_4)_3$.

3) Addition of silica to the top of the slag does not have any effect in lowering the copper content.

4) A mixture of 50 pct pyrites and 50 pct silica removes copper from the upper layers of slag, but the effect is not appreciably greater than by settling alone.

5) Converter slag behaves in a similar way to the reverberatory slag and the same trends are noticeable.

6) The reduction of magnetite in all cases is very rapid, but copper removal is much slower.

No attempts were made to explain these results or to apply them in actual operations. Reduction of magnetite by silica or pyrite is a well-known and accepted fact,[5, 6] but in the case of the present experiments, it was felt that the reaction with the crucible walls (referred to earlier) may also have played a part. It is also known that magnetite, and the copper locked up in it, can be settled out mechanically. Present results have, therefore, confirmed what has already been reported by other workers,[5, 6] namely, that reducing agents such as pyrites or carbon (in this case from the crucible walls) reduce the magnetite content of slags and free the locked-up copper and that the settling effect on slags also is very beneficial, while silica when added to the top surface is not very effective but may probably be much more so when thoroughly mixed with the slag.

It may be difficult to apply these relatively well-known remedies in practice in a plant of old design and working under severe space limitations. Settling of slags either requires external settlers or can be done in the reverberatory itself, but only at the expense of severely reducing output, and the addition of reducing agents either in the converter slag ladle or through the roof of the reverberatory is not likely to be very effective.

Full Scale Test on Reverberatory Slag

Small scale tests provide indications, but full scale work is necessary to confirm them. Facilities for carrying out such work are not always available, especially when the plant is working to capacity. Arrangements were made, however, with the operating department for a full scale test of 24 hr. This period was selected as the holding capacity of each furnace is approximately 600 to 700 tons of charge, giving a *residence time* of 18 to 20 hr, so that conditions should be fairly stabilized after 24 hr. In any case, 24 hr was the maximum the operators were able to allow for this particular test.

No change was made in the feed to either furnace. All the converter slag was put in No. 2 reverberatory, leaving No. 1 reverberatory free of converter slag for a full day. During each tapping of the slag, samples were taken at 5-min intervals from No. 1 furnace and at 15-min intervals from No. 2 furnace. The copper and magnetite assays on the composites of these samples are shown in Figs. 4 and 5, where the time intervals and duration of slag taps are also indicated.

It was not possible to alter the charge composition to No. 1 furnace to compensate for the absence of the highly basic converter slag and, as was to be expected, slag conditions became distinctly viscous after about 20 hr and there was considerable siliceous mushy material floating on the slag, although temperature was well maintained at about 1250°C. This condition disappeared soon after normal charging of converter slag was resumed. On the other hand, No. 2 furnace ran very fluid and rather on the hot side throughout the test run owing to the unusual quantities of high temperature converter slag passing through it.

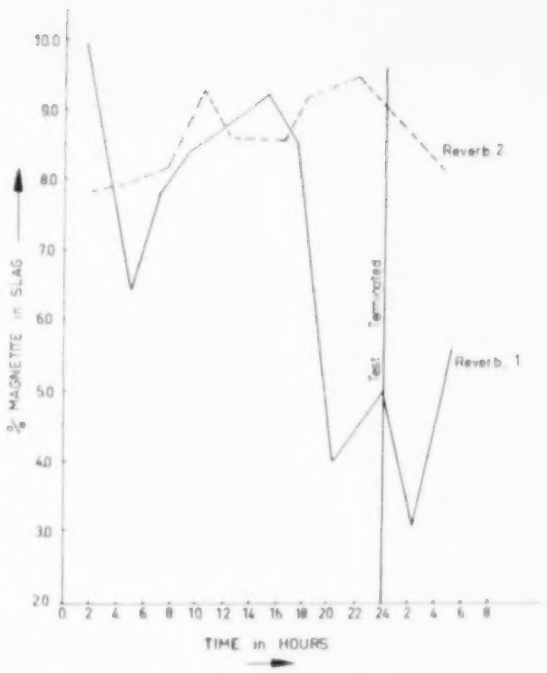

Fig. 5—Special 24 hr reverberatory run. Reverberatory No. 1 was without converter slag; reverberatory No. 2, with twice the usual amount of converter slag.

The rapidity with which conditions returned to normal after restoring the usual converter slag feed to No. 1 furnace confirms the suspicion that converter slag tends to run straight through the reverberatory to the slag end, although at the same time dropping some of its magnetite and copper on the way. It is hoped that at some future date it will be

Table VIII. Converter and Reverberatory Slag, Ammonia-Ammonium Carbonate Leaching*

Total Pressure, Psi	Temperature, °C	Time, Min	Wt of Slag, G	Ml of NH_4OH, 15.1 Normal	$(NH_4)_2CO_3$, G	NH_3, Concentration of G per Liter	Extraction of Cu, Pct
70	90	120	100	140	100	75.5	60.0
100	100	120	100	140	100	75.5	84.8
250	150	120	100	140	100	75.5	70.7
140	140	90	100	140	100	75.5	70.7
140	140	120	100	140	100	75.5	74.5
200	125	120	100	140	100	75.5	75.7
150†	125	120	100	140	100	75.5	86.5
150	125	60	100	140	100	75.5	77.8
150	125	120	100	140	100	75.5	91.3
150	125	120	100	175	50	60.0	91.2
150	125	120	100	196	20	61.0	89.9
150	125	120	100	107	20	36.5	77.4
150	125	120	200	140	50	56.5	75.0
150‡	125	120	200	140	50	56.5	86.9
150‡	125	120	200	140	50	56.5	93.0

* In all the above experiments the total volume was brought up to 1 liter by the addition of distilled water. All of the experiments were carried out in an oxygen atmosphere. Oxygen pressure at the start of the experiment (room temperature) was 80 psi.

† Optimum temperature, pressure, and leaching time.

‡ Converter slag was used in all tests in the above tabulation except the last two, which were based on reverberatory slag.

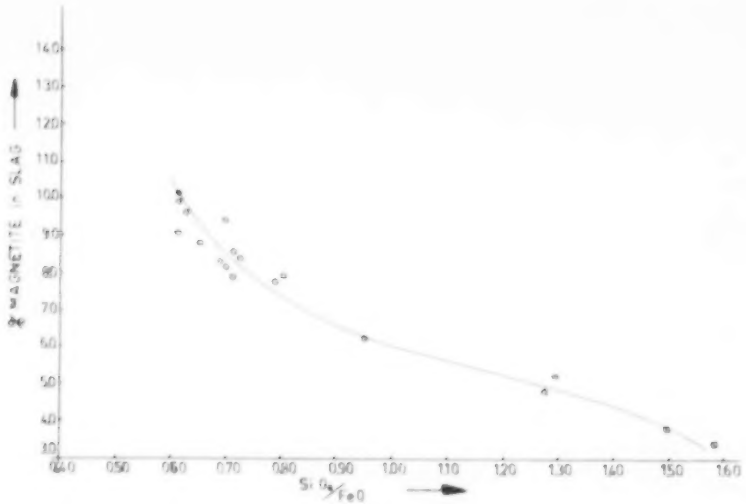

Fig. 6—SiO_2/FeO ratio vs magnetite content in reverberatory slag during special 24 hr reverberatory run.

possible to investigate this further by the use of radioactive tracers, which should prove a valuable aid in tracking down copper losses in slags.

It was noticed that the copper and magnetite contents in reverberatory No. 1 showed a definite downward trend, while in reverberatory No. 2 the magnetite remained more or less constant and the copper content significantly increased, see Figs. 4 and 5. These results prove that high magnetite content and copper losses in reverberatory slags are partly related to the presence of converter slag in the reverberatory furnace. Fig. 6 shows the relation between the SiO_2/FeO ratio and the magnetite content. Considering Figs. 4 through 6 together leads to the conclusion that there is a definite relation between the SiO_2/FeO ratio, the magnetite, and the copper contents of the reverberatory slag.

In Table V an attempt was made to summarize the results obtained during this run as far as slag losses are concerned. It is not claimed that the material balances presented are very accurate, but they are reliable as far as copper losses in the slags are concerned. The second material balance is a computed one, calculated from slag conditions obtained in No. 1 furnace after 20 hr test run when steady conditions were reached. It is clearly shown that daily copper losses are reduced from 6.08 tons to 2.00 tons. However, this does not show how to recover copper from the converter slag if this is removed from the smelting circuit. In the following section tentative methods are indicated by which this copper could be recovered, and it has been possible in laboratory tests to obtain 93 pct extraction of the copper contained in converter slags. The copper balance then looks as shown in Table VI.

It should also be considered that the reverberatory capacity may be considerably increased by diverting converter slags, and that furnace life would be prolonged. However, it would be necessary to alter the charge composition and there would be less scope for the direct smelting of oxidized ores with a high silica gangue.

Treating Copper Slags by Leach Methods

Consideration has been given to the recovery of copper from slags by a separate treatment. At first magnetic separation was tried, but the magnetite was so finely disseminated as to make the method unworkable. Similarly, flotation of copper sulfide in reverberatory slags gave recoveries of less than 50 pct, even at low grades of concentrates. Therefore, these results are not being presented in detail, although a fair amount of work was done.

This led to the investigation of leach methods. Laboratory work in this respect has gone forward along three lines:

1) A double leaching process, first with dilute sulfuric and then with acidified ferric sulfate solution, has yielded satisfactory results on both the converter and reverberatory slags.

2) Pressure leaching of the slags with ammonia and ammonium carbonate in an oxidizing atmosphere seems to yield very good results at relatively low pressures and temperatures.

3) At higher pressures and temperatures a dilute sulfuric solution was found to be very successful in extracting copper from the slags. Again, the presence of an oxidizing atmosphere is necessary.

In all these processes, extraction of copper from both the converter and reverberatory slags runs higher than 90 pct on an average. Some of the results are shown in Tables VII and VIII.

Acknowledgments

Thanks are due to R. P. Koenig, President of the Cerro de Pasco Corp., and to A. H. Engelhardt, Vice-President and Manager of Operations of the Sierra Div. in Peru, for permission to publish this paper. The authors are indebted to N. Manrique, Chief Research Chemist, Oroya, for the considerable help given in painstakingly analyzing several hundred slag samples. Thanks are also due to G. C. Amstutz, Petrologist, for the microscopic work done on copper slags and for the photographs presented in this paper. Any study of this kind, conducted largely in the plant, depends chiefly on the willing help and cooperation of the plant personnel, for which the authors are very grateful.

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Preparation and Properties of Boron Treated Nonaging Open Hearth Steel

The high ductility and nonaging characteristics of boron treated low carbon open hearth steels have been demonstrated both in laboratory tests and in commercial deep drawing applications. The addition of more than 0.005 pct B, in the form of ferroboron, seriously affects the rimming characteristics of most low carbon open hearth steels. In order to achieve the desired total of 0.007 pct B required to avoid strain aging and yet not suppress rimming, it is best to use at least 0.004 pct B as a capping addition. The efficiency of the boron addition is greatest when it is added prior to the aluminum cap in a chemically capped steel. Nitrogen strain aging can be completely eliminated in such steels. At the same time an ingot to slab yield of 85 pct can be combined with an increased ductility.

by Eric R. Morgan and John C. Shyne

WHEN temper rolled low carbon sheet is stored at room temperature before use, changes take place in its mechanical properties. This phenomenon is known as *strain aging*.

Normally these changes are observed by means of Olsen ductility and Rockwell *B* hardness tests but unfortunately such tests are relatively insensitive. Strain aging can be readily observed in the laboratory by means of tensile tests. The tensile test method is even more sensitive if the aging is allowed to take place in specimens which have been prestrained in tension rather than by cold rolling. In fact one of the great benefits of commercial temper rolling is that it introduces a residual stress pattern which tends to mask the effects of strain aging when the sheet is finally used in a pressing operation.

Curves *B*, *C*, and *D* of Fig. 1 illustrate the changes that take place during the aging of commercial rimmed steel at room temperature following straining in tension, curve *A*, Fig. 1. The first important change that can be observed is an increase in the stress required to produce plastic flow. This increase is, in this paper, called the *aging index*. As aging proceeds and the aging index increases, there is also an observable return of the yield point, an increase in the ultimate tensile strength, and a decrease in elongation to fracture.

The results of strain aging in deep drawing steel manifest themselves as stretcher strains (Lüders bands), buckling, and tearing. In deep drawn parts such effects are undesirable and strain aging is a serious problem. The rate of strain aging of a steel depends upon its composition and prior mechanical and thermal history, but for most temper rolled open

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TP 4437CE. Manuscript, Aug. 2, 1956. New Orleans Meeting, February 1957.

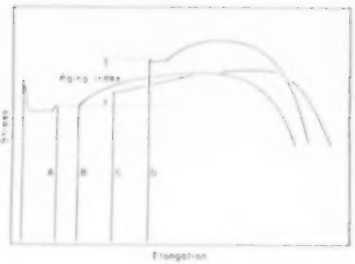

Fig. 1—Schematic diagram of tensile tests for strain-aged rimmed steel. *A* refers to tensile pre-strain; *B*, unaged; *C*, aged three days at 76°F; and *D*, aged 30 days at 76°F.

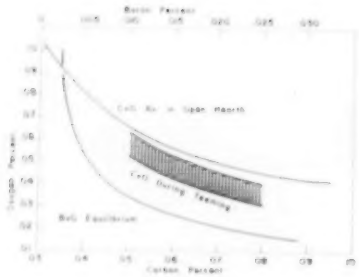

Fig. 2—B-O and C-O relationships in molten steel.

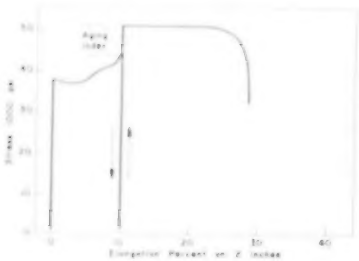

Fig. 3—Tensile test curve for strain-aged steel C1, containing 0.000 pct B, and aged 14 days at 76°F.

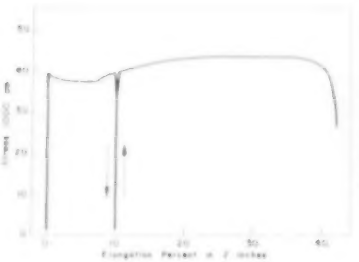

Fig. 4—Tensile test curve for strain-aged steel C7, containing 0.008 pct B, and aged 14 days at 76°F.

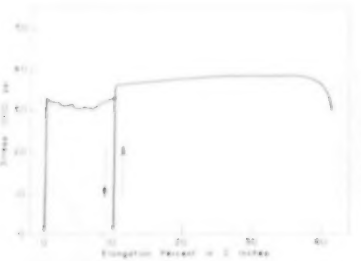

Fig. 5—Tensile test curve for strain-aged steel C14, containing 0.002 pct B, and aged 14 days at 76°F.

hearth rimmed steels, strain aging is well advanced and observable in three or four days of storage.

A previous investigation by Morgan and Shyne[1] had shown that strain aging could be eliminated from certain steels which contained boron. The following work concerns the progress of that idea toward the development of a practical commercial nonaging open hearth steel suitable for deep drawing applications.

Principles of Strain Aging

The most satisfactory theory of strain aging is that due to Cottrell.[2] This theory suggests that strain aging may be regarded as the migration of interstitial solute atoms, such as carbon and nitrogen, to free dislocations and the resultant anchoring of those dislocations. The important factor which governs the degree of strain aging in a given storage time at room temperature is the effective amount of carbon and nitrogen in solution.

In order to produce a strong yield point in temper rolled steel there must be, according to the Cottrell theory, at least 0.001 wt pct C + N in solution. This amount is considerably in excess of the total equilibrium solubilities of carbon (10^{-4} pct) and nitrogen (2×10^{-3} pct) at room temperature. In practice the commercial annealing of steels leads to considerable supersaturation of carbon and nitrogen. The degree of supersaturation of nitrogen is far greater than that of carbon, so that in open hearth steels nitrogen is the most important cause of strain aging. Commercially processed open hearth steel may contain as much as 0.004 pct N in solution after annealing.

The amount of nitrogen in solution can be limited by the addition of strong nitride forming elements such as aluminum or titanium,[3] but this has the disadvantage that it leads to a killed steel. Vanadium[4] is effective in eliminating nitrogen strain aging from rimmed steels, but it is too expensive an alloying addition. Morgan and Shyne[1] have shown that boron can also eliminate nitrogen strain aging from laboratory steels of commercial composition. Boron is, however, a mild deoxidizer[5] and the object of the present work was to determine the effectiveness of boron in eliminating nitrogen strain aging from commercial open hearth steels without suppressing rimming.

Table I. Results of Boron Additions to Rimming Steel Ingots, Heat A*

Boron, Pct Added	Form of Boron Addition	Aluminum, Pct Added	Rimming Action	Ingot Characteristic
0.000	—	0.005	Good	Normal
0.003	Ferroboron	0.004	Slightly retarded	Normal
0.003	Boron Carbide	0.004	Slightly retarded	Normal
0.004	Ferroboron	0.004	Slightly retarded	Normal
0.004	Boron Carbide	0.004	Slightly retarded	Normal
0.005	Ferroboron	0.004	Slightly retarded	Heavy slag and bleeding
0.005	Boron Carbide	0.004	Slightly retarded	Heavy slag and bleeding
0.0075	Ferroboron	0.004	Retarded	Heavy slag and bleeding
0.010	Ferroboron	0.004	Seriously retarded	Growing and bleeding
0.015	Ferroboron	0.004	Nil	Semikilled
0.020	Ferroboron	0.004	Nil	Semikilled

* Composition at teeming, 0.060 pct C and 0.044 pct O.

Table II. Effect of Boron Addition Technique on Boron Content of Ingot, Heat C*

Ingot No.	Boron, Pct in Mold	Boron, Pct in Cap Prior to Aluminum	Boron, Pct in Cap with Aluminum	Analyzed Boron, Pct at Ingot Center	Rimming Condition	Ingot to Slab, Yield Pct	Aging† Index	Total Elongation in 2 In.
1	—	—	—	0.000	Good	90	8050	29
2	0.002	—	—	0.002	Slightly retarded	89	7500	32
3	0.004	—	—	0.004	Slightly retarded	89	7500	32
4	0.003	0.005	—	0.006	Slightly retarded	89	5650	36
5	0.003	0.005	—	0.008	Slightly retarded	89	0	42
6	0.004	0.004	—	0.007	Slightly retarded	88	0	41
7	0.004	0.004	—	0.008	Slightly retarded	88	0	42
8	0.003	—	0.005	0.005	Slightly retarded	80	0	43
9	0.003	—	0.005	0.003	Slightly retarded	82	0	42
10	0.004	—	0.004	0.005	Slightly retarded	71	0	41
11	0.004	—	0.004	0.003	Slightly retarded	70	3100	42
12	—	—	0.008	0.001	Good	76	5200	37
13	—	—	—	0.000	Good	82	6900	36
14	—	0.007	—	0.002	Good	83	1600	42

* Steel containing 0.07 pct C and 0.043 pct O as teemed. An addition of 0.004 pct Al was made to each mold during teeming.
† The increase in flow stress produced by prestraining 10 pct (in 2 in.) and aging for 14 days at 76°F.

Table III. Effect of Rimming and Capping Techniques on Boron Contents of Various Heats*

Heat No.	Boron, Pct in Mold	Aluminum, Pct in Mold	Rimming	Boron, Pct in Cap	Aluminum, Lb in Cap	Ingot Condition	Ingot to Slab, Yield Pct	Analyzed Boron, Pct in Ingot			Analysis as Teemed	
								Top	Center	Bottom	Pct C	Pct O
A	0.005	0.004	Slightly retarded	—	10	Normal	84	—	0.005	—	0.06	0.044
	0.010	0.004	Retarded	—	10	Light bleeding	83	—	0.007	—		
B	0.010	0.004	Retarded	—	10	Heavy bleeding	85	—	0.002	—	0.06	0.065
	0.010	—	Retarded	—	10	Bleeding	87	—	0.005	—		
	0.0075	—	Slightly retarded	—	10	Normal	86	0.004	0.006	0.003		
	0.005	0.004	Slightly retarded	—	10	Normal	87	—	0.003	—		
C	0.004	0.004	Slightly retarded	—	10	Normal	89	—	0.004	0.003	0.07	0.043
	0.004	0.004	Slightly retarded	0.004	10	Normal	88	—	0.008	0.004		
	—	0.004	Good	0.007	10	Normal	83	—	0.002	0.001		
D	0.004	0.004	Slightly retarded	0.004	10	Overcapped	74	0.011	0.011	0.007	0.05	0.050
E	0.004	—	Slightly retarded	0.004	6	Heavy bleeding	85	0.006	0.004	0.004	0.065	0.050
	0.004	—	Slightly retarded	0.004	8	Medium bleeding	86	0.005	0.005	0.003		
	0.004	—	Slightly retarded	0.004	10	Light bleeding	85	0.006	0.005	0.005		
F	0.004	—	Slightly retarded	0.004	8	Normal	85	0.005	0.005	—	0.06	0.052
	0.004	—	Slightly retarded	0.004	9	Normal	85	0.004	0.004	—		
	0.004	0.002	Slightly retarded	0.004	10	Normal	85	0.006	0.004	0.004		
	0.004	—	Slightly retarded	0.004	11	Normal	85	0.007	0.003	—		
G	0.004	0.003	Slightly retarded	0.004	10	Normal	85	0.004	0.004	0.003	0.065	0.042
	0.004	0.002	Slightly retarded	0.004	10	Normal	85	0.004	0.004	0.003		
	0.004	—	Slightly retarded	0.004	11	Normal	85	0.004	0.004	—		

* All boron capping additions were made prior to aluminum capping.

Boron in Rimming Steel

The important advantages of a rimmed steel over a killed steel are its relatively pure iron rim, its high ingot to slab yield, and its lower cost to produce. Having a relatively pure iron surface endows it with superior surface properties in the finished sheet form.

The rimmed surface region results from the rejection of dissolved carbon and oxygen from the solidifying metal and their subsequent combination and removal as gaseous CO. This reaction is termed rimming. Rapid evolution of gas ensures a satisfactorily thick rimmed skin but less vigorous rimming can lead to gas cavities near the surface of the solidified ingot. Overvigorous rimming leads to deep contraction of the ingot top and a poor yield. It is important that the amount of oxygen and carbon be controlled so as to give suitable rimming conditions. A satisfactory C-O product (i.e., [%O] [%C]) for rimming is 0.0026 to 0.0030.

At tap the open hearth steel contains an excess of oxygen as compared with equilibrium conditions. This excess of oxygen is reduced somewhat during tapping and holding prior to teeming, Fig. 2, but still exceeds the equilibrium amount. The excess of oxygen can be readily controlled by the judicious addition of aluminum to the mold during teeming.

Fig. 2 also shows the equilibrium relationship between oxygen and boron in molten steel, as determined by Derge.[5] According to this data, the oxygen content of 0.047 pct usually found in a 0.06 pct C steel during teeming could exist in equilibrium with 0.007 pct B. This means that mold additions of 0.007 pct or less of boron would not be expected to combine with the oxygen in a typical 0.06 pct C steel and affect the rimming action. This boron content is exactly that shown by Morgan and Shyne[6] to be most effective in suppressing aging in laboratory melts.

Boron additions in the form of ferroboron (17.5 pct B) and boron carbide (45 pct B) were made, during teeming, to rimming ingots prepared from an open hearth heat. The results are given in Table I.

In those ingots in which the rimming action was noted to be slightly retarded, a gradual improvement in rimming action was detected after about 1 min. Those ingots which were rimmed showed a low boron yield and were aging, whereas the semikilled ingots were nonaging with a high boron yield.

The addition of boron carbide was not as satisfactory as an addition of ferroboron because it was difficult to dissolve and gave a lower boron yield in the finished steel. All subsequent mention of boron additions will refer to the use of ferroboron, unless otherwise stated.

Boron in Chemically Capped Steel

A chemically capped ingot is one which is initially allowed to rim in the usual manner but is subsequently semikilled by the addition of a deoxidizer

such as aluminum. This type of steel then combines the desirable rimmed surface characteristic of rimming steel with the high ingot to slab yield characteristic of semikilled steel. It was anticipated that the partial deoxidation achieved during chemical capping would minimize the oxidation of the boron addition and thus result in a higher addition efficiency.

The successful preparation of chemically capped steel depends upon a satisfactory initial rimming period, so that the effect of boron upon rimming is important. Additions of ferroboron and boron carbide were made to the molds during teeming of another heat (heat *B*) and it was observed that 0.0075 pct B had only a slightly retarding effect upon rimming. The composition of the steel at teeming was, however, 0.06 pct C and 0.065 pct O. This C-O product (0.0039) was abnormally high, so that the removal of some oxygen by the boron was not so deleterious to rimming. On the basis of these first two experiments and the results of Derge,[4] it was decided that no more than 0.004 pct B should be added if satisfactory rimming was to be obtained in all future heats.

This value of 0.004 pct B is appreciably lower than the optimum value of 0.007 pct recommended by Morgan and Shyne.[3] Therefore, the possibility of adding the extra boron as a capping addition was investigated. There appeared to be two reasonable ways of adding boron as a capping addition so as to give a good boron distribution in the ingot. The extra boron could be distributed only if it were added to turbulent metal and therefore it had to be added either prior to or with the normal aluminum capping addition. These two addition techniques were applied and the results are given in Table II.

The lower ingot to slab yield for ingots 8 to 14 of this heat (heat C) can be accounted for by the fact that overheating occurred during the soaking operation. Further work has shown that boron treated ingots are no more prone to soft centers than similarly heated steels without boron.

Table IV. Strain Aging Characteristics of Boron Treated Steels Produced from Ingots Showing Normal Capped Characteristics

Ingot No.	Aging Treatment	Aging* Index	Ultimate Tensile Strength, Psi	Total Elongation, Pct in 2 In.	Analyzed Boron Content, Wt Pct
C1	Annealed	—	46900	40	Nil
	14 days, 76°F	8050	51100	29	
	30 days, 76°F	7600	51300	29	
	1 hr, 212°F	7850	52000	28	
C6	Annealed	—	45000	42	0.007
	14 days, 76°F	0	45750	41	
	30 days, 76°F	0	45000	41	
	1 hr, 212°F	0	44900	40	
C8	Annealed	—	43850	42	0.005
	14 days, 76°F	0	44800	43	
	30 days, 76°F	0	43700	43	
	1 hr, 212°F	0	43900	43	
B1	Annealed	—	43950	44	Nil
	14 days, 76°F	5600	44850	32	
	30 days, 76°F	5900	45300	32	
	1 hr, 212°F	6850	47500	35	
B4	Annealed	—	42350	44	0.006
	14 days, 76°F	0	41900	41	
	30 days, 76°F	0	42750	42	
	1 hr, 212°F	0	43150	42	
B5	Annealed	—	41850	43	0.004
	14 days, 76°F	0	43250	42	
	30 days, 76°F	0	42800	43	
	1 hr, 212°F	0	43250	41	

* The increase in flow stress produced by prestraining 10 pct and aging.

The total elongation (in 2 in.) of the untreated steels was 40 pct in the unaged (annealed) condition, whereas those boron treated steels which were nonaging exhibited a total elongation of 42 pct even after strain aging at room temperature for 14 days. This higher ductility of the nonaging boron treated steels was a generally observed phenomenon. Typical stress-strain curves for some of these steels are given in Figs. 3, 4, and 5. The results also show that there was no appreciable decrease in ductility on aging until the aging index had exceeded 3500 psi.

The amount of aging which can be tolerated will vary from application to application. However, it is safe to assume that a steel which does not demonstrate an aging index of more than 2000 psi will not exhibit stretcher strains in any pressing operation.

In the preparation of ingot 4 the capping addition was not stirred, whereas in the preparation of ingots 5, 6, and 7 the capping additions were thoroughly stirred in. The importance of this stirring is demonstrated by the absence of aging in ingots 5, 6, and 7.

In the case of the mixed ferroboron and aluminum capping addition, stirring was difficult because of the tendency for the mixture to sinter and form a cake. This difficulty was most apparent for ingots 11 and 12. It is significant that the boron yield was always lower in those ingots prepared by this technique.

The completely successful nonaging ingots 5, 6, and 7 plus the almost successful ingot 14, all produced by boron capping prior to aluminum capping, suggested that this was the best capping technique.

It is surprising that ingots 11 and 14, which contained no more than 0.003 pct B, were nearly nonaging even under the exaggerated aging test conditions used. However, it must be appreciated that the suggested optimum[3] value of 0.007 pct B was based on experimental alloys containing more nitrogen than the present open hearth steel. A reasonable figure for the minimum safe boron content in the present open hearth steel appears to be about 0.004 pct.

The important boron content is not necessarily the total boron present but rather that boron which is effectively free to combine with the dissolved nitrogen. Any boron present as boron oxide will not contribute to the formation of the B-N complex.

If some of the boron is oxidized after it is added to the mold and it floats to the top to form a slag or is mechanically entrapped, the amount of effective boron present in the ingot should depend largely upon the capping practice. An efficient aluminum capping addition should reduce this boron oxide rich slag to boron which can be reabsorbed by the

Table V. Results of Boron Treated and Regular Steel Processed into Mercury Door Panels

Ingot No.	Analysis, Boron Pct in Ingot	Storage Period in Days	Performance
A6	0.005	4	No stretcher strains
		35	No stretcher strains
A7	0.007	4	No stretcher strains
A4	Nil	14	Severe stretcher strains, required roller leveling
A2	Nil	4	Light stretcher strains, required roller leveling
		35	Severe stretcher strains, required roller leveling

remaining liquid steel. At the same time the removal of oxygen from the molten steel should result in the reduction of the boron oxide which is mechanically suspended in the turbulent metal. This would increase the efficiency of the boron addition.

The effects of variations in capping practice were studied and some of the results are summarized in Table III.

Several conclusions may be drawn from these results:

1) The boron yield was highest when the degree of deoxidation was greatest, as in heat *D*. In this case a normal capping practice of 10 lb Al led to overcapping and deeply piped ingots because of the low C-O product of the steel as teemed.

2) Even when the ingot was not sufficiently deoxidized in capping, as in heat *E*, there was a relatively high boron yield within the ingot. However, subsequent testing showed that those ingots which were subject to bleeding also exhibited some aging.

3) The implication is that when capping does not sufficiently depress the free oxygen content of the steel, the boron will not exist in an effective form.

4) All ingots containing more than 0.004 pct analyzed boron and showing normal capped characteristics, such as a flat top or slight crown after capping, were completely nonaging under all test conditions. Examples are given in Table IV.

In order to obtain successful boron treated nonaging ingots it is essential that the oxygen content of the steel be controlled within certain limits. This is probably best achieved by using only those heats which will be tapped at not less than 0.06 pct C. At that carbon level, the C-O product will usually fall within the satisfactory limits of 0.0026 to 0.0030 at teeming. A standard preparation technique can then be applied with reasonable assurance that normal ingots will be produced.

Laboratory tensile tests showed that the largest boron additions used did not impair the ductility of low carbon sheet steel. This was also borne out by Olsen ductility and Rockwell hardness results. Boron apparently dissolves in cementite[7] and does not form another precipitate phase which can interfere with plastic deformation.

Table VI. Results of Regular and Boron Treated Steel Processed into Ford Front Fenders

Ingot Type	Scrap Parts, Pct	Repaired Parts, Pct	Storage Period in Days
Regular chemically capped	2.1	15.7	2
Boron treated, chemically capped	1.9	8.2	2

Rolling and Annealing Procedures

Experience has shown that boron treated steel can be soaked and slabbed in the same way as untreated steel of the same grade. Under normal soaking conditions steels containing boron are identifiable from the apparent scale blisters all over the surface. There was no greater tendency for surface defects or ingot crumble for the treated material than for untreated material.

The reheated slabs were hot stripped to finish at 1540°F and then coiled at a variety of specified temperatures. There was no obvious difference produced by coiling at temperatures within the range 1100° to 1300°F.

All commercial coils were cold reduced 60 pct after pickling because laboratory tests had shown this to be satisfactory. Annealing cycles normally used for regular chemically capped steel were adopted with success. The material showed only normal sensitivity to variations in annealing practice. An annealing temperature of 1320°F is recommended.

Boron treated, chemically capped material has shown good ductility and low hardness and has been satisfactory for use on the most severe deep drawing operations.

Boron Treated Steel in the Stamping Plant

The obvious benefits of a nonaging steel lie in the absence of stretcher strains and the retention of its high ductility throughout prolonged storage. In order to study the susceptibility of boron treated steel to stretcher strain formation a quantity of this material was processed into Mercury door panels. This part requires only a shallow draw so that any tendency toward the formation of stretcher strain would have been obvious. The results are given in Table V.

The storage period of five weeks used for this test spanned the record period of hot weather of the summer of 1955. It is significant that the boron treated steel showed no signs of aging.

In order to study the effects of boron treatment on the ductility of finished sheet steel a considerable quantity of boron treated material was tested by drawing into Ford front fenders. The results of this test are given in Table VI.

When processed as freshly temper rolled material the boron treated steel showed definite superiority in the form of a lower percentage of scrap and split parts. These results confirm the conclusion from laboratory tests that boron improves rather than detracts from the ductility of low carbon open hearth steel in addition to imparting nonaging characteristics.

Acknowledgments

The authors wish to express their thanks to the many colleagues who offered assistance and encouragement, particularly to H. W. Clark, S. McNairn, R. Martin, and J. Ingall. Grateful acknowledgment is also due to K. D. Cassidy, General Manager, Steel Div., and A. A. Kucher, Director, Scientific Laboratory, Ford Motor Co., for permission to publish this work.

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Reduction of Nickel by Hydrogen from Ammoniacal Nickel Sulfate Solutions

This paper is an account of a detailed examination of the reaction by which nickel can be precipitated from aqueous ammoniacal nickel sulfate solutions by hydrogen at elevated pressures and temperatures. The thermodynamics of the reactions are discussed and the behavior of ammonia is illustrated. A mechanism is proposed to account for the catalytic effect of ferrous salt additions, and the effect of variables on the autocatalytic nature of the reduction is described with particular reference to the dependence of the reaction rate on the available surface area of nickel metal.

by V. N. Mackiw, W. C. Lin, and W. Kunda

IN the process employed by Sherritt Gordon Mines Ltd. for the production of metallic nickel, a sulfide concentrate is leached with ammonia and air under pressure. Following the removal of iron, copper, and other impurities, there remains a purified solution having the following analysis: 40 to 50 g per liter Ni, 200 to 400 g per liter $(NH_4)_2SO_4$, and 20 to 30 g per liter NH_3. Metallic nickel is reduced from this solution by hydrogen under pressure at 300° to 350° F in mechanically agitated autoclaves.

A catalyst, ferrous sulfate, is required to initiate the first reduction. After the reduction, the depleted solution is discharged, leaving the metallic nickel in the autoclave. The nickel produced, being in a finely divided form, is used as a catalyst for the reduction of the next batch of solution. Upon repeated use the metallic nickel particles increase in size and become more compact, resulting in the production of a powder with higher apparent density. For this reason, each reduction is termed *densification*. Finally, when the burden of metal powder in the autoclave becomes too great to obtain effective agitation, both powder *and* depleted solution are discharged. The autoclave is then filled with fresh solution, ferrous sulfate catalyst added as before, and a new cycle started. The operation is described in earlier publications.[1,2]

A comprehensive historical review of the reduction of metals from solutions in general was given in a paper by Schaufelberger.[3]

The experimental data presented in this paper were taken from the work done in the Research Laboratory of Sherritt Gordon Mines Ltd. in Ottawa during the development of the process in 1951 and 1952. The results of the work were tested on a pilot plant scale in Ottawa in the period 1952 to 1953. Following laboratory and the pilot plant studies a commercial process has operated successfully since 1954 in the Nickel Refinery of Sherritt Gordon Mines Ltd. in Fort Saskatchewan, Alberta.

General Experimental Technique

The experiments were carried out in a stainless steel, 1-gallon, agitated autoclave designed and manufactured by Autoclave Engineers Inc. The inside dimensions of the vessel were 5 in. diam and 12 in. depth.

The stirrer consisted of a ½ in. diam shaft 11 in. long fitted with an axial flow type impeller (three blades bent to throw downwards) and a radial flow

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TP 4442D. Manuscript, May 9, 1956. New York Meeting, February 1956.

four straight blade impeller placed 3 in. above. Both impellers had a diameter of 2½ in. The stirrer was rotated at 730 rpm* except as otherwise stated.

* A rotation speed of 730 rpm for the arrangement used was found to be normally above the critical speed. Below the critical speed, the mass transfer would become the rate controlling factor.

A 2.5 liter charge was placed in the autoclave, which was then closed and purged with hydrogen. The rotation of the stirrer was started and the solution heated with an external burner. The temperature was measured by a thermocouple fitted into a thermowell through the head of the autoclave. When

Table I. Relation between Temperature and Reaction Rate

Temperatures			Reciprocal of Absolute Temperature, $\frac{1}{T}$	$t_{½}$, Min	Rate Constant, $\frac{100}{t_{½}}$, Min^{-1}
°F	°C	°T			
300	149	422	0.00237	64	1.56
325	163	436	0.00229	38	2.63
350	177	450	0.00222	23	4.35
375	191	464	0.00216	18.5	5.40
400	204	477	0.00210	15	6.67

the required reaction temperature was reached, the pressure gage indicated the vapor pressure of the solution. Hydrogen was admitted through an opening on the head to a total pressure equal to the vapor pressure plus the desired hydrogen partial pressure. During the reduction, samples were drawn at convenient time intervals for analysis.

The data referred to in Figs. 13, 14, and 15 were collected from experiments carried out in a 2 ft diam by 7 ft long horizontal autoclave with three vertical impellers.

Thermodynamic Considerations

The chemical reactions involved in the reduction of nickel by hydrogen in ammoniacal solutions are

$$Ni^{++} + H_2 \rightleftharpoons Ni + 2H^+ \quad [1]$$

$$H^+ + NH_3 \rightleftharpoons NH_4^+ \quad [2]$$

$$n = 1 \text{ to } 6 \quad [Ni(NH_3)n-1]^{++} + NH_3 \rightleftharpoons [Ni(NH_3)n]^{++}. \quad [3]$$

According to Eq. 2, increasing NH_3 concentration favors the forward reaction in Eq. 1 while, according to Eq. 3, it retards the forward reaction in Eq. 1 by reducing the simple Ni^{++} concentration.

A semiquantitative treatment to illlustrate this dual effect of NH_3 is as follows:

a) The redox potential of the system H^+/H_2 is given by* $E = -0.060\ pH - 0.030 \log a_{H_2}$ at 30°C, where a_{H_2} is the activity of hydrogen. At constant ionic strength, and assuming a direct proportionality between the solubility and the partial pressure of H_2,

$$E = E_1 + 0.060 \log [H^+] - 0.030 \log p_{H_2} \quad [4]$$

where E_1 is the potential at unit H^+ concentration and unit H_2 pressure, $[H^+]$ is the hydrogen ion concentration, and p_{H_2} is the hydrogen partial pressure.

b) The redox potential of the system Ni(II)*/Ni

* Ni(II) is used to indicate bivalent nickel whether or not it is complexed with NH_3.

is* $E = E^0 + 0.030 \log a_{Ni^{++}}$ at 30°C, where $a_{Ni^{++}}$ is the activity of Ni^{++} and the activity of nickel metal is set equal to 1.

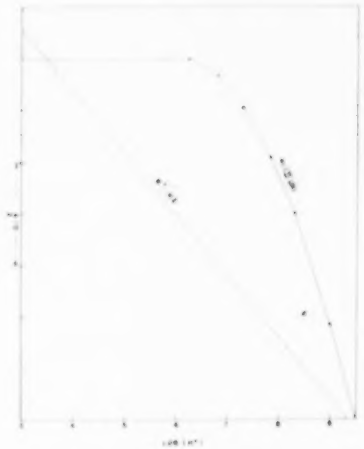

Fig. 1—Redox potentials at various pH's in ammoniacal nickel salt solutions.

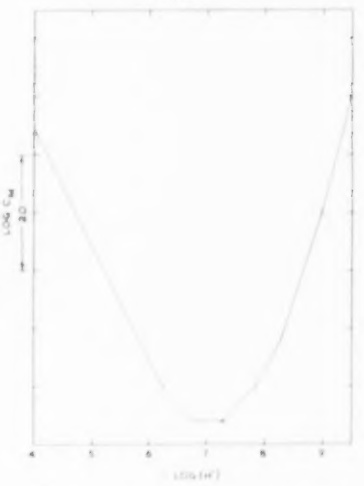

Fig. 2—Logarithms of equilibrium concentrations of nickel at various pH's in ammoniacal salt solutions in presence of H_2.

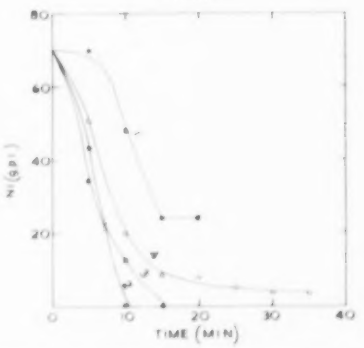

Fig. 3—Reduction of nickel at various initial NH_3/Ni ratios; nickel metal powder used as catalyst. Numbers refer to initial NH_3/Ni ratio (molar).

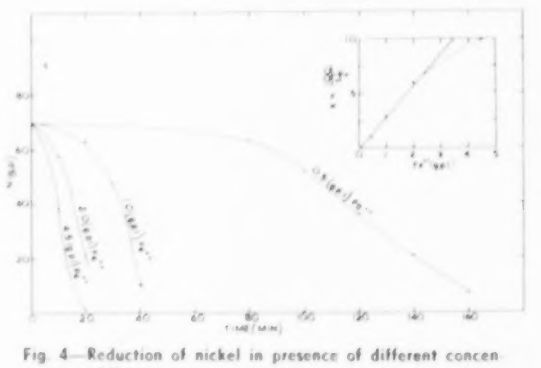

Fig. 4—Reduction of nickel in presence of different concentrations of Fe^{++}.

At constant ionic strength

$$E = E_0 + 0.030 \log [Ni^{++}] \quad [5]$$

where E_0 is the potential at unit Ni^{++} concentration, and $[Ni^{++}]$ is the concentration of Ni^{++} in solution. In ammoniacal solutions, some of the nickel ions are bound to ammonia molecules so that the concentration of Ni(II) in solution is

$$C_{Ni} = [Ni^{++}] + [NiNH_3^{++}] + [Ni(NH_3)_2^{++}] + \cdots + [Ni(NH_3)_n^{++}]$$

where all the terms are concentrations. At constant ionic strength

$$\frac{[Ni(NH_3)n^{++}]}{[Ni(NH_3)n-1^{++}][NH_3]} = k_n$$

$$C_{Ni} = [Ni^{++}](1 + k_1[NH_3] + \cdots + k_1k_2k_3k_4k_5k_6[NH_3]^6). \quad [6]$$

By combining Eqs. 5 and 6

$$E = E_0 + 0.030 \log \frac{C_{Ni}}{1 + k_1[NH_3] + \cdots + k_1k_2k_3k_4k_5k_6[NH_3]^6}. \quad [7]$$

The values of k_1, k_2, ..., k_6 can be taken from Bjerrum's[5] results. For instance, in 2 molar ammonium nitrate, at 30°C, log k_1 equals 2.80; log k_2 2.24; log k_3 1.73; log k_4 1.19; log k_5 0.75; and log k_6 0.03. Under these conditions

$$\frac{[H^+][NH_3]}{[NH_4^+]} = 10^{-9.26}$$

becomes

$$[H^+][NH_3] = 10^{-9.26} \quad [8]$$

Combining Eqs. 7 and 8

$$E = E_0 + 0.030 \log \frac{C_{Ni}}{1 + \frac{10^{-9.26}}{[H^+]} + \frac{10^{-18.52}}{[H^+]^2} + \cdots}$$

or

$$E = E_0 + 0.030 \log C_{Ni} - 0.030 \log \left[1 + \frac{10^{-9.26}}{[H^+]} + \frac{10^{-18.52}}{[H^+]^2} + \cdots\right]. \quad [9]$$

Between certain values of (H^+), the following approximations may be made

$$\left.\begin{array}{ll} -\log [H^+] < 6.23 & E = E_0 + 0.030 \log C_{Ni} \\ 6.23 < -\log [H^+] < 6.79 & \\ & E = E_0 + 0.030 \log C_{Ni} - 0.030 \log \dfrac{10^{-9.26}}{[H^+]} \\ 6.79 < -\log [H^+] < 7.30 & \\ & E = E_0 + 0.030 \log C_{Ni} - 0.030 \log \dfrac{10^{-18.52}}{[H^+]^2} \end{array}\right\} \quad [10]$$

The redox potentials of the systems Ni(II)/Ni and H^+/H_2 may now be plotted against $-\log [H^+]$, see Fig. 1, using Eqs. 4 and 10.

The position of the Ni(II)/Ni curve relative to the H^+/H_2 curve is not fixed owing to the unknown quantities, E_1 and E_2. Increasing the hydrogen partial pressure p_{H_2} would lower the position of the H^+/H_2 curve. A change in temperature within the normal range would change the slopes of both curves only slightly and to the same extent. The shapes of the two curves are such that, at extreme pH values, the forward reaction is not possible while, in the intermediate range, where the Ni(II)/Ni curve is above the H^+/H_2 curve, the forward reaction will proceed.

An alternative approach to the same problem can be made by equating Eqs. 4 and 9 to obtain an expression for the equilibrium metal concentration, C_{Ni}, as a function of $-\log [H^+]$ and p_{H_2}

$$E_1 + 0.030 \log C_{Ni} - 0.030 \log \left[1 + \frac{10^{-9.26}}{[H^+]} + \cdots\right] = E_2 + 0.060 \log [H^+] - 0.030 \log p_{H_2}$$

or

$$\log C_{Ni} = \frac{E_2 - E_1}{0.030} + 2 \log [H^+] + \log \left[1 + \frac{10^{-9.26}}{[H^+]} + \cdots\right] - \log p_{H_2}. \quad [11]$$

Log C_{Ni} is plotted against $-\log [H^+]$ in Fig. 2. Again the quantities E_1, E_2, and p_{H_2} will fix the absolute position of the curve. The concentration of Ni(II) at equilibrium is therefore minimum between $-\log [H^+] = 6.79$ and 7.30, when nickel is mainly present in solution as $Ni(NH_3)_2^{++}$ ions. No experimental equilibrium concentration data are available to illustrate the foregoing theoretical discussion. The data given by Schaufelberger[7] correspond only to the left hand side of the curve in Fig. 2. They showed the slope of the *log* C_{Ni} *vs pH* curve to be −2, in agreement with the theory developed. Later work in the Sherritt Gordon Mines laboratory, when both nickel and cobalt were present in solution, also showed a slope of −2 for either the *log* Ni^{++} *vs pH* or *log* Co^{++} *vs pH* curves,[8] for the low pH range.

Effect of Ammonia

In practice, it has been found that when there are, in the original solution, 2 mol NH_3 per mol Ni, the latter may be completely reduced; at the end of the reduction, all the NH_3 is neutralized by the H^+ generated. In the case where there is less than the stoichiometric amount of NH_3 present in the original solution, when all of the NH_3 is neutralized the pH of the solution drops and the reduction stops before all the nickel is reduced. When there are more than 2 mol NH_3 per mol Ni present originally, as the reduction proceeds the ratio of concentration of NH_3 to nickel increases. The complexing of more of the simple Ni^{++} results, and a point is reached where the Ni^{++} concentration is so low that the reaction stops.

A series of experiments serves to illustrate this point. Solutions containing 70 g per liter Ni were prepared for the reduction experiments using nickel ammonium sulfate. The initial NH_3/Ni molar ratios used were 1, 2, 3, and 4. The temperature of reaction was maintained at 400°F and the total pressure at 640 psig, corresponding to approximately 400 psi H_2. The 100 g per liter metallic nickel with the following screen analysis was used as a catalyst: −100 + 150 mesh, 5.1 pct; −150 + 200 mesh, 6.3 pct; −200 + 325

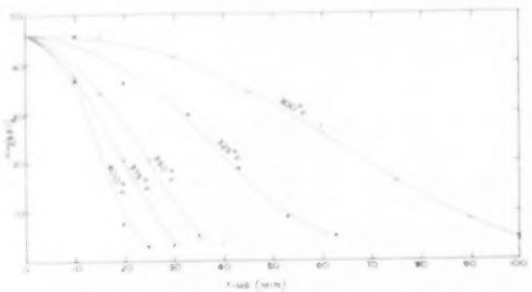

Fig. 5—Reduction of nickel at various temperatures with Fe^{++} catalyst.

mesh, 16.3 pct; and −325 mesh, 72.3 pct; total, 100 pct.

The data are plotted in Fig. 3. The graph shows that not all the nickel was reduced when the starting concentration of NH_3 was much higher than that required for neutralizing the acid formed during the reduction. It also shows the abrupt ending of the reaction when the initial NH_3 concentration was very much below the stoichiometric requirement. In the experiments that follow, the initial NH_3/Ni ratio was about 2.

Reactions Involving Ferrous Sulfate as Catalyst

During the development of the process in the research laboratory of Sherritt Gordon Mines Ltd., it was discovered that the addition of a ferrous salt to the solution not only catalyzed the reduction of nickel by hydrogen, but also resulted in the production of a very fine and active nickel powder. Later it was found that with increasing concentrations of $(NH_4)_2SO_4$, the catalytic effect of ferrous salt decreased. Experiments were therefore carried out to determine the effects of the concentration of ferrous ion, the reaction temperature, and the $(NH_4)_2SO_4$ concentration on the rate of nickel reduction employing $FeSO_4$ as a catalyst.

In this study the solution used was prepared with aqueous ammonia and nickel ammonium sulfate to give a nickel concentration of 70 g per liter and a NH_3/Ni molar ratio of 2. The temperature was maintained at 400°F and the total pressure at 650 psig,

Table II. Relation Between $\frac{W_t}{W_i}$ and $\frac{A_t}{A_i}$

$\frac{W_t}{W_i}$	$\frac{A_t}{A_i}$
1.1	1.07
1.25	1.16
1.5	1.31
2.0	1.59

corresponding to a partial pressure of H_2 of about 400 psi. The agitator speed was 640 rpm. The data are plotted in Fig. 4.

A plot of $\frac{100}{t\frac{1}{2}}$ (a measure of the rate constant, k) vs g per liter Fe^{++} present is shown in the insert of Fig. 4. The $t\frac{1}{2}$ (half life time) is the time required for reduction of 50 pct of the nickel in solution. Approximately direct proportionality can be seen between this rate constant and the catalyst concentration. This is in agreement with catalytic reactions in general. At the very high Fe^{++} concentrations of 4.5 g per liter, the rate of reaction probably was limited by the rate of mass transfer.

Effect of Temperature

The effect of temperature on the rate of reaction using Fe^{++} as catalyst can be illustrated by the following series of experiments.

The solution used (for this set of experiments) was prepared from aqueous ammonia and nickel ammonium sulfate to give 80 g per liter Ni and 46 g per liter NH_3 (NH_3/Ni molar ratio of 2). $FeSO_4$ at 1.2 g per liter Fe^{++} was added as a catalyst. The partial pressure of H_2 was maintained at 350 psi for all experiments. In these experiments the NH_3 titrations instead of the nickel analyses were used to follow the progress of the reaction. This is justifiable

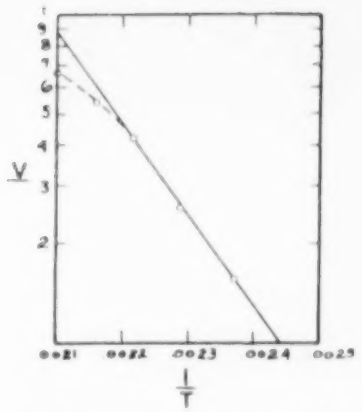

Fig. 6—Log K vs $1/T$ plot; Fe^{++} catalyst.

because for each mol of nickel reduced 2 mol NH_3 are neutralized.

The data are plotted in Fig. 5. From the figure, the $t\frac{1}{2}$ values and their reciprocals may be read and calculated. These values and the corresponding temperature functions are given in Table I.

The plot of log k vs $\frac{1}{T}$ as shown in Fig. 6 does not give a straight line owing probably to many factors, of which the variation of H_2 solubility with temperature is one. The solubilities of H_2 in water at various temperatures and under constant partial pressures of H_2 have been determined.[7,8] If the same temperature coefficient of solubility change is assumed for the solutions used, corrections on the reaction rates may be made. However, the corrections were found to be small except for temperatures above 400°F. Therefore, instead of making the corrections, an apparent effect of temperature on the reaction rate (including the solubility effect) was determined for two temperature ranges, 300° to 350°F and 350° to 400°F. At higher temperatures, other factors such as mass transfer might have caused a slower than expected rate. Thus, the apparent energy of activation ranges from 13.7 kcal at 300° to 350°F to 6.5 kcal at 350° to 400°F.

Kinetics of the Reaction Involving Fe^{++} Catalyst

The shapes of the curves shown in Figs. 4 and 5 are found to be close to parabolic except toward the end of the reaction. A plot of nickel (or NH_3) concentrations against the square of time should therefore give a straight line.

Since there were not enough experimental points for plotting, readings were taken from the top portions of the curves in Fig. 5. The values of NH_3 concentration are plotted against the values of $(t)^2$ in Fig. 7.

The parabolic nature of the rate curves can be explained if the following assumptions are made:

1) The rate of reduction is directly proportional to the number of *nuclei* formed.

2) The rate of formation of the *nuclei* is constant.

Therefore

$$\frac{dc}{dt} = k'N \qquad [a]$$

$$\frac{dN}{dt} = k'' \qquad [b]$$

where c equals concentration of nickel (or NH_3) in

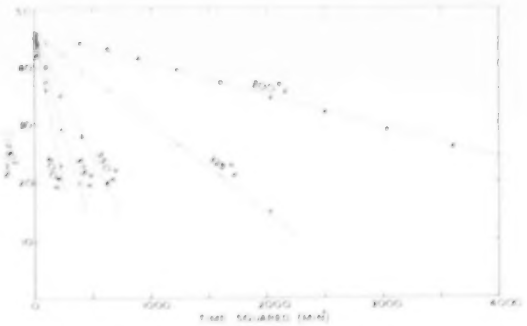

Fig. 7—NH_3 concentration vs t^2 plot, Fe^{++} catalyst.

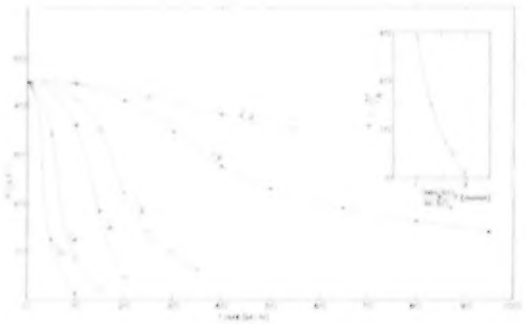

Fig. 8—Effect of $(NH_4)_2SO_4$ on rate of reduction with Fe^{++} catalyst. Numbers indicate initial $(NH_4)_2SO_4$: $NiSO_4$ ratio (molar).

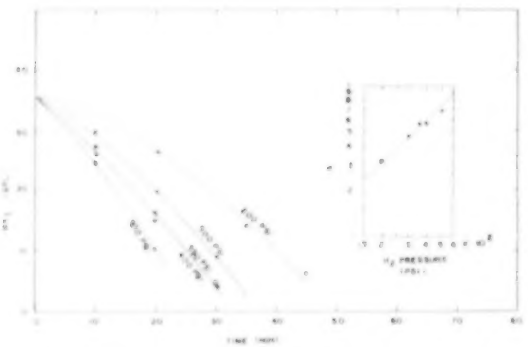

Fig. 9—Reduction of nickel at various H_2 pressures; nickel metal powder used as catalyst.

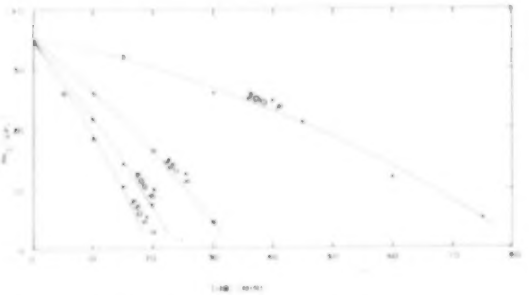

Fig. 10—Reduction of nickel at various temperatures; nickel metal powder used as catalyst.

solution, N equals number of *nuclei*, and t equals time.

From Eq. b, $N = k''t$, and from Eq. a, $-\frac{dc}{dt} = k'k''t$. Therefore, $c = c_o - \frac{k'k''}{2}t^2$ or $c = kt^2$, where $k = \frac{k'k''}{2}$.

The slowing of the rate toward the end of the reaction can be explained by a process whereby the number of *nuclei* decreases by the agglomeration of the very fine (microscopic or submicroscopic) particles to form macroscopic particles. The significance of this phenomenon will be illustrated further later on.

Effect of $(NH_4)_2SO_4$ and a Hypothesis to Explain The Mechanism of the Fe^{++} Catalyst

The addition of $(NH_4)_2SO_4$ to a reaction system using Fe^{++} catalyst was found to retard the reaction. The reaction cannot proceed if the concentration of ammonium sulfate in solution exceeds a certain critical value. This critical concentration depends upon other solution conditions.

One series of experiments illustrates this point. The solutions used contained 45 g per liter Ni and 26 g per liter NH_3 (NH_3/Ni molar ratio = 2) and different concentrations of $(NH_4)_2SO_4$; 1 g per liter Fe^{++}, added as $FeSO_4$, was used as a catalyst. A temperature of 300°F and a partial pressure of H_2 of 400 psi were maintained. The results of the experiments are plotted in Fig. 8. A plot of the reciprocal of $t\frac{1}{2}$ values against the initial $(NH_4)_2SO_4/NiSO_4$ molar ratios is given in the insert in Fig. 8.

The results of Fig. 8 show that the rate is strongly dependent on the $(NH_4)_2SO_4$ concentration and above a certain concentration the rate is infinitely slow. By extrapolating a curve of $\frac{100}{t\frac{1}{2}}$ vs $(NH_4)_2SO_4$, see insert in Fig. 8, it can be shown that at an initial ratio of 2 (for 45 g per liter Ni) the time becomes infinite. In the last experiment, all the metal reduced was plated on the wall of the vessel, indicating that in this particular case only the walls were acting as a catalyst.

Table III. Relation between Temperatures and Rate Constants

Temperatures °F	Temperatures °C	Temperatures °T	$\frac{1}{T}$	$t\frac{1}{2}$, Min	$k \sim \frac{100}{t\frac{1}{2}}$, $t\frac{1}{2}$ Min^{-1}
300	149	422	0.00237	53	1.9
350	177	450	0.00222	19	5.3
400	205	478	0.00210	13	7.7
450	232	505	0.00198	11	9.1

It was noticed that in cases of low $(NH_4)_2SO_4$ concentrations, a turbidity was obtained when $FeSO_4$ was added, while in cases of very high $(NH_4)_2SO_4$ concentrations, the solutions remained clear. These observations suggest that at low $(NH_4)_2SO_4$ concentrations $Fe(OH)_2$, which probably is responsible for the catalysis, is formed. The metallic nickel nuclei formed initially then behave autocatalytically. The $(NH_4)_2SO_4$ concentration increases as the reaction proceeds and, when it is too high for the $Fe(OH)_2$ to be stable, the latter dissolves and the acceleration

stops. All the iron added was finally found in the solution in the Fe^{++} state.

Autocatalytic Nature of Nickel Reduction

In the preceding paragraph, the kinetics of nickel reduction catalyzed by FeSO, have been discussed. The following discussions will concern the kinetics of nickel reduction when metallic nickel is present as a catalyst.

Metallic nickel is known to activate hydrogen and is used as a hydrogenation catalyst. Since metallic nickel is the product of the reduction reaction under discussion, it is understandable that the reaction should become autocatalytic; that is, the reaction should accelerate and the order of reaction should be negative (even when metallic nickel is the only catalyst present).

In practice, however, it has been found both in the laboratory and in the plant that, as a rule, when only metallic nickel is used as a catalyst, the rate

Table IV. Relation between Surface Areas and Reaction Rates

No. of Densification, i	Average Particle Diameter, a, $2r$		Wt of Nickel Catalyst per Liter, G, W	Total Surface Area, $M^{\dagger}$, $A^{\dagger}$	Reduction Time, Min, t	Rate Constant, Min^{-1} $\frac{100}{t}$
	Observed	Corrected*				
1		26	60	2.0	80	1.25
2	27.4	32	105	2.2	101	0.99
3	42.1	38	150	2.7	91	1.10
4		45	195	2.9	84	1.19
5	47.3	50	240	3.2	75	1.33
6	57.0	55	285	3.5	67	1.49
7		60	330	3.7	75	1.33
8	67.6	64	375	4.0	70	1.43
9	66.3	67	420	4.2	57	1.75
10		70	465	4.5	58	1.72
11	68.8	73	510	4.7	52	1.92

* These are values taken from a smooth curve drawn through the experimental points shown in Fig. 13.

† $A = \frac{W}{4/3\pi r^3 d}(4\pi r^2) = \frac{3W}{rd}$, where d is the density of nickel, 8.9 g per cu cm.

curve is essentially linear; i.e., the reaction is of the zero order. Exceptions have been observed, but usually they can be explained by the particular experimental conditions employed.

A zero order curve corresponds to a catalytic reaction in which the concentration of the catalyst does not change during the reaction. Since one of the products of reaction is metallic nickel, the total catalytic surface increases as the reaction proceeds. However, as will be shown later, the reduced nickel deposits on the surface of the nickel already present, causing a growth of the solid particles. For spherical particles, it can be shown that the ratio of final surface to initial surface is equal to the $\frac{2}{3}$ power of the

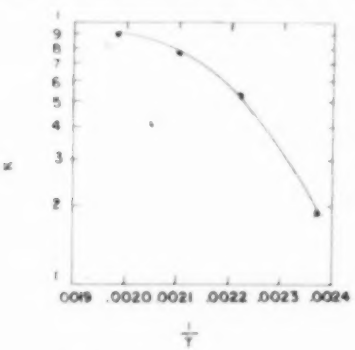

Fig. 11—Log K vs $1/T$ plot; nickel metal powder used as catalyst.

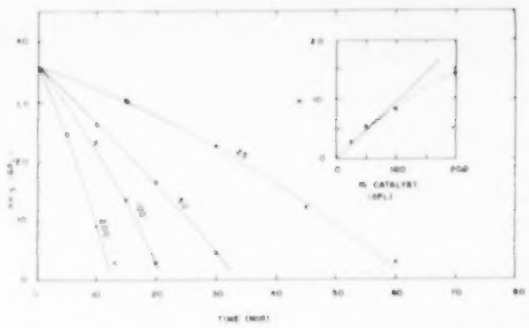

Fig. 12—Effect of nickel catalyst concentration on reduction rate.

ratio of final weight to initial weight. Thus

$$\frac{A_f}{A_i} = \left(\frac{W_f}{W_i}\right)^{\frac{2}{3}}$$

where A_f is the final surface area; A_i the initial surface area; W_f, the final weight; and W_i, the initial weight.

Table II gives the relation between $\frac{A_f}{A_i}$ and $\frac{W_f}{W_i}$ for a range of $\frac{W_f}{W_i}$ values commonly encountered, i.e., from $\frac{W_f}{W_i} = 1.1$ to 2.0.

Assuming a direct proportionality between the reaction rate and the surface area, it can be seen that if the deposited weight is less than one quarter of the original weight of metallic nickel, the increase in surface or rate of reaction is less than 16 pct. The curvature is therefore not large enough for the curve to appear as deviating appreciably from a straight line.

Factors which cause the curve to deviate considerably from a straight line are numerous. Among those which cause a change in the reaction order toward the positive side, i.e., a deceleration of the reaction, are:

1) The use of nickel powder approaching the critical size for maintaining suspension under given agitation conditions. (In this case, the growth of the nickel particles in the course of the reduction causes them to settle to the bottom of the autoclave, thereby lowering the effective catalytic surface area.)

2) Depletion of Ni^{++} toward the end of the reaction so that the effect of its concentration becomes more pronounced. (This is especially true when starting with a NH_3/Ni molar ratio greater than 2.)

3) The tendency of very fine nickel particles to agglomerate, causing a decrease in the catalytic surface.

One of the factors which causes a change in the reaction order toward the negative side, i.e., an acceleration of the reaction, is the initial gradual establishment of the equilibrium between hydrogen gas, dissolved hydrogen, and adsorbed hydrogen.

Experience in pilot plant scale reduction runs has shown that, after an original nickel catalyst has been used a few times with a solution containing 2 mol NH_3 per mol Ni, the reduction curves always show a zero order form, i.e., the rate is constant from the beginning to the end.

In laboratory scale experiments, linear (or nearly linear) reduction curves are also obtained within a rather wide range of conditions.

Dependence of Rate of Reduction on Hydrogen Pressure

A series of experiments to determine the effect of H_2 pressure was carried out using solution with the following analysis: 54 g per liter Ni, 35 g per liter NH_3, and 360 g per liter $(NH_4)_2SO_4$.

For catalyst, 50 g per liter Ni with an apparent density of 0.6 g per cu cm was used. The temperature was 350°F. The NH_3 concentrations were used to follow the progress of reduction. The data are plotted in Fig. 9, showing the curves to be very close to straight lines.

A log-log plot of pressure vs k, see insert in Fig. 9, gave a slope of 0.9. Therefore, the relationship may be written as $k \sim (p_{H_2})^{0.9}$.

The rate of reduction is almost directly proportional to the partial pressure of hydrogen.

Temperature Coefficient of the Rate of Reduction

A series of reduction experiments with nickel powder as catalyst was made to determine the effect of temperature on the rate of reduction. The solution and the nickel catalyst used were the same as those described in the above series of experiments. The partial pressure of H_2 was kept at 350 psi. The data are given in Fig. 10.

The curves again are quite linear. The temperature functions, the $t_{\frac{1}{2}}$ values, and their reciprocals are given in Table III.

A plot of $\log k$ vs $\frac{1}{T}$ as shown in Fig. 11 for the estimation of the energy of activation shows that a straight line is not obtained. Again, since the solubilities of gases vary with temperature under equal pressures, only an apparent temperature coefficient of reaction rate can be obtained. Thus, for the same ranges of temperatures as chosen previously, we have the apparent energy of activation equal to 13.7 kcal at 300° to 350°F, and 5.7 kcal at 350° to 400°F.

The similarity between these activation energy values and those calculated for the Fe^{++} catalyzed reaction for the same temperature ranges indicates that, in the latter reaction, the rate of formation of *nuclei* is probably not temperature sensitive.

Dependence of Rate on the Nickel Catalyst Concentration

A series of experiments to determine the effect of nickel catalyst concentration was carried out. The solution contained 54 g per liter Ni, 36 g per liter NH_3, and 440 g per liter $(NH_4)_2SO_4$. Various quantities of metallic nickel catalyst (apparent density = 0.6 g per cu cm) were used. The temperature was 350°F and the H_2 partial pressure, 350 psi.

The reduction rates are plotted in Fig. 12, and the rate constant K vs nickel catalyst concentration is plotted in the insert of Fig. 12.

The rate constant is seen to be approximately directly proportional to the nickel catalyst concentration. The diminishing effect at higher concentrations might be due to the difficulty of maintaining larger quantities of metallic nickel in suspension.

Dependence of Reaction Rate on the Surface Area Of The Nickel Catalyst and the Growth Pattern of The Nickel Particles During Reduction

The direct proportionality between the reaction rate and the weight concentration of catalyst has been indicated when the latter is of the same degree of fineness. It remains to be shown that the reaction rate is proportional to the surface area regardless of the fineness of the catalyst particles.

In one pilot plant scale operation (run No. 23, cycle No. 16) carried out in 1952, a quantity of nickel catalyst (15 g per liter) was prepared and used for 11 successive reductions (called *densifications*), reducing 45 g per liter Ni each time. A sample of the metal was withdrawn after each densification for microscopic measurement of the particle diameters. The particles in the first five densifications of a cycle were quite spherical and uniform in size. An apparent surface area of a single particle could, therefore, be deduced. From the total weight of metal, the number of particles could also be calculated and thus the total apparent surface area. The times required for the complete reduction, the reciprocals of which serve as a measure of the reaction rates, were obtained from the Operational Log Book.

The pertinent data are combined and given in Table IV.

The rate constant expressed as $\frac{100}{t}$ is plotted against the total apparent surface area in Fig. 14. An approximate direct proportionality between the two can be readily seen.

The total weight of the nickel catalyst after a certain number of densifications, i, may be written as $W_i = W_0 + iW$, where W_0 is the original weight of the catalyst, W is the weight of the nickel deposited in each densification, and i is the number of densifications. The total weight may also be expressed as $W_i = \frac{4}{3}\pi r^3 nd$, where r is the average radius of the particles, n is the number of particles, and d is the density of nickel. Equating the two expressions above, $W_0 + iW = \frac{4}{3}\pi r^3 nd$, or $r^3 = \frac{3}{4\pi nd}(W_0 + iW)$.

A plot of r^3 against the number of densifications, i, should give a straight line, with a slope equal to $\frac{3W}{4\pi nd}$ if n is constant. An actual plot is illustrated in Fig. 15.

There is a deviation from the straight line at the start corresponding to the initial four or five densifications. This initial curved portion has an increasing slope, $\frac{3W}{4\pi nd}$, with increasing i indicating that n decreases, for it is known that W is constant and

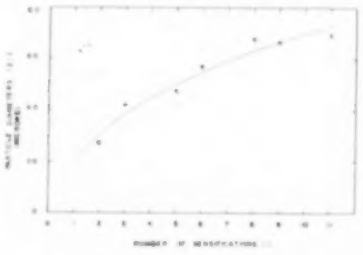

Fig. 13—Growth of nickel particles.

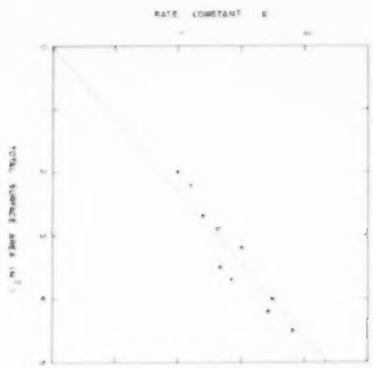

Fig. 14—Dependence of rate on catalytic surface area.

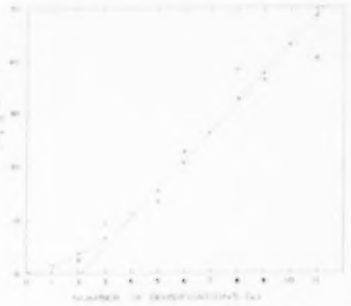

Fig. 15—Growth of nickel particles (r^3 vs t). Closed circles refer to interpolated values, open circles, experimental values.

that d, the density, is either constant or can only increase till it reaches the density of solid nickel. A comparison of the number of particles at $i = 1$ and at $i = 5$ gives a ratio of 4. Thus, the process of agglomeration, which results in a decrease in the number of particles at the end of a nickel reduction in which Fe^{++} is used as a catalyst, probably continues in the early densifications when the particles are still fine. The critical size of the particles at which agglomeration ceases depends on many factors, of which degree of agitation is probably very important.

Summary

Both theory and practice show that the reduction of nickel proceeds to completion only when the NH_3/Ni molar ratio is in the range of about 1.5 to 2.5.

The reaction is catalyzed by Fe^{++}, resulting in the formation of metallic nickel nuclei, which further catalyze the reaction, causing an acceleration of the reaction rate (autocatalysis). The acceleration may be explained by assuming a constant rate of formation of the *nuclei* and a direct proportionality between the rate of reduction and the number of the nuclei.

The nuclei probably not only grow during reduction, but also agglomerate into larger sized particles and gradually assume the spherical form. When a certain critical size is reached, the agglomeration process ceases and the particles grow symmetrically in all directions. At this stage, the rate of reduction is found to be directly proportional to the calculated surface area of the nickel particles.

Apart from the effect of catalysts, the reaction rate is found to be proportional to the H_2 partial pressure to the first order (approximate), to be independent of the nickel concentration in solution, and to have an apparent energy of activation of between 5 and 15 kcal.

Acknowledgments

The authors wish to thank Sherritt Gordon Mines Ltd. for providing the opportunity and encouragement to work on this problem and for permission to publish the results. They wish to express their gratitude to F. A. Forward and the late S. Nashner for their interest and support of the work, to thank J. Halpern for his contribution to the treatment of the kinetics of the Fe^{++} catalyzed reaction, R. L. Benoit for his contribution to the treatment of the thermodynamics of the reduction of nickel in ammoniacal solutions, and J. P. Auffray for his part of the work on the nickel particle growth problem.

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Discussion of this paper sent (2 copies) to AIME by Aug. 1, 1957 will appear in AIME *Transactions* Vol. 212, 1958, and in JOURNAL OF METALS, October 1958.

Technical Note

Bismuth in Copper Grain Boundaries

by C. W. Spencer, R. A. Rummel, and F. N. Rhines

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TN 407E. Manuscript, Nov. 30, 1956.

SPECIMENS of five cast Cu-Bi alloys, containing 4.68, 0.53, 0.043, 0.0064, and 0.0025 wt pct Bi and cast pure copper were subjected to a bend test to determine their relative ductility. Using metallographic methods the structures of the fractured surfaces were compared with those of the polished cross sections. Embrittlement was found to be associated with the presence of a second phase in the grain boundaries although, in the lower bismuth

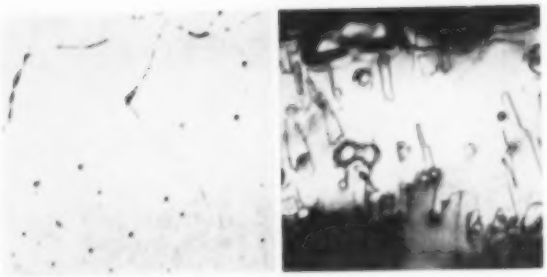

Fig. 1—0.53 pct Bi in copper. a) LEFT: Intercrystalline bismuth in the polished cross section. Electropolished in an orthophosphoric acid solution (1.35 specific gravity) using a voltage of 1.9 to 2.0 volts, and etched in a 10 pct solution of ammonium persulfate. X500. b) RIGHT: Intercrystalline bismuth on the fractured cross section. The small outlined areas are the remnants of the bismuth film. X1050. Reduced approximately 25 pct for reproduction.

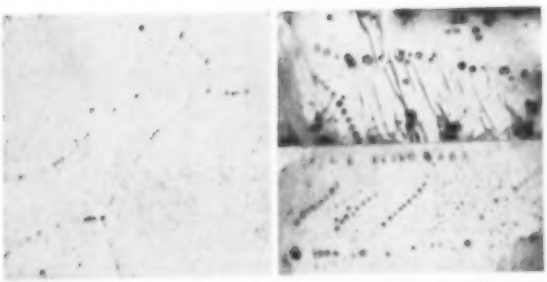

Fig. 2—0.043 pct Bi in copper. a) LEFT: Intercrystalline particles of bismuth in the electropolished and etched cross section. X500. b) RIGHT: Composite of two areas on the fractured cross section showing particles of bismuth. X1050. Reduced approximately 25 pct for reproduction.

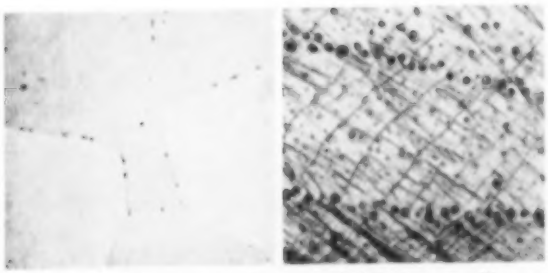

Fig. 3—0.0064 pct Bi in copper. a) LEFT: Intercrystalline particles of bismuth in the electropolished and etched cross section. X500. b) RIGHT: Particles of bismuth on the fractured cross section. X1050. Reduced approximately 25 pct for reproduction.

content alloys, the second phase was in the form of small lenticular particles rather than as a continuous film separating the grains.

The alloys were prepared by melting electrolytic copper and a Cu-Bi master alloy in a graphite crucible under borax. Cylindrical test specimens 2½ in. long and 3/16 in. in diam were machined from cast bars ½ in. in diam; the average grain diameter was approximately 0.01 in.

The specimens were held in a vise and subjected to 45° reversed bends until failure. The results are shown in Table I.

Table I. Experimental Results

Alloy Composition, Wt Pct Bi	4.68	0.53	0.043	0.0064	0.0025	Pure Copper
45° Reversed Bends to Failure	~0.1	~0.5	1-2	7	18	22

In the two alloys of highest bismuth content, 4.68 and 0.53 pct Bi, bismuth is distributed as continuous films on some grain boundary surfaces while on others it is distributed as discrete particles of lenticular shape. These two modes of distribution are illustrated in Fig. 1a, taken of the polished and etched structure of the 0.53 pct Bi alloy. The dark circular particles are bismuth trapped in the interior of the copper grains during solidification. An area on one face of a fracture of this alloy is shown in Fig. 1b. The slightly darker and somewhat irregularly shaped areas are fragments of a bismuth film which adhered to this face. Under white light these areas appear as light blue patches against a bright copper background.

Only discrete particles of the bismuth-rich phase are found in the 0.043 pct Bi alloy, the polished structure of which is Fig. 2a. The particles, as exposed on the fracture of a specimen of this alloy, appear as shown in Fig. 2b, which is a composite of two areas on the fracture.

Similar polished and fractured cross sections of the 0.0064 pct Bi alloy are shown in Figs. 3a and 3b, in which fewer bismuth particles are present. Only infrequently were bismuth particles observed on the fracture of the 0.0025 pct Bi alloy. In texture, this fracture resembles that of the pure copper.

There has been disagreement as to whether the embrittling effect of bismuth in low bismuth content alloys is due to the presence of a submicroscopically thin film of bismuth in the grain boundaries or to a temper-brittleness effect resulting from the segregation of bismuth, without precipitation, in the vicinity of the grain boundaries.[1-5] The above structures, although they tend to support Samules' conclusion that thin intercrystalline films are not present in low bismuth content alloys, associate embrittlement with the presence of a second phase in the form of small particles in the copper grain boundaries.

Acknowledgment

The authors wish to thank The International Nickel Co. Inc. for supporting this work and for performing the chemical analyses of the alloys.

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Dissolution of Lead Sulfide Ores in Acid Chlorine Solutions

The rate of reaction of chlorine in aqueous solutions with galena is first order and both sulfate and elemental sulfur can be formed, the latter via the hydrolysis of sulfur chloride which adheres to the ore. At temperatures above 45°C the reaction is transport-controlled, but at room temperature mixed chemical and transport control operates. The chemical rate constants have been evaluated and the energy of activation found to be 21,000 cal per mole. Under certain conditions the formation of sulfur is zero order with respect to chlorine, although the reaction also has an activation energy of 21,000 cal per mole. From quantitative kinetic data the conditions for maximum production of sulfate or sulfur can be predicted.

by M. I. Sherman and J. D. H. Strickland

PRELIMINARY experiments in these laboratories showed that whereas pyrite[1] produced only sulfate the action of aqueous chlorine solutions on most other sulfide ores resulted in the formation of a mixture of sulfate and elemental sulfur, the production of the latter being favored by a very dilute solution of oxidant. The reactions taking place were obviously complex and only a detailed kinetic study could be expected to clarify the position and enable a prediction to be made of conditions leading to the rapid formation of metal salt and the economically desirable elemental form of sulfur. Galena was chosen for the first investigation as it is of widespread occurrence and is representative of a simple cubic lattice sulfide containing the monosulfide unit, $S^{=}$.

Experimental Procedure

The apparatus and general technique used in this work have already been described.[1] Analyses for chlorine and sulfate were carried out by the same methods as those used for pyrite. The lead in 1 ml aliquots of solution was determined polarographically, after destroying chlorine with hydrazine hydrochloride and making solutions 0.5 molar with hydrochloric acid.

A large sample of Kansas galena, assaying at better than 98 pct PbS, was crushed and wet sieved to give fractions of −10 + 14, −20 + 28, −28 + 35, and −48 + 65 Tyler screen. The particles were almost perfect cubes and the apparent surface per gram was calculated assuming each particle a cube of side equal to the mean mesh opening. A volume *shape factor*, calculated as for pyrite, was exactly unity.

The main apparatus was unsuitable for direct visual examination of the ore particles during the reaction. For this purpose a small cell from a Spekker Absorptiometer (optical flats 1 cm apart) was closed by a greased microscope slide after filling with oxidant solution. One or two ore particles were placed in the cell and the solution was stirred by a glass covered speck of iron wire activated by an external rotating magnet. The surface of an ore particle was examined under a binocular microscope at between 10 and 40 magnifications.

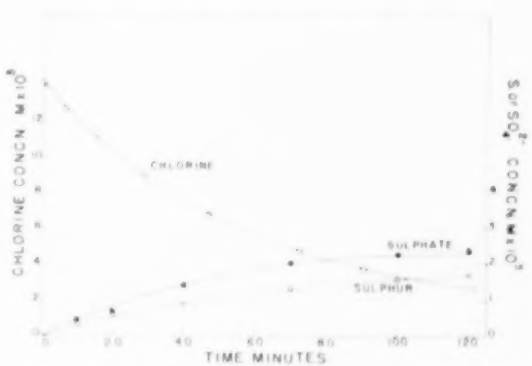

Fig. 1—Change of chlorine, sulfate, and sulfur concentration with time for 56 sq cm of galena. Solution at 25°C, stirred at 300 rpm.

Results

Experiments were made under a wide variety of conditions, the form of presentation of the data being illustrated by Fig. 1, where the concentrations of chlorine, sulfate, and sulfur are plotted against time.

The fictitious *concentration* of solid sulfur is used for convenience and is the molarity of sulfur which would be recorded if the elementary sulfur formed during the reaction were dissolved in the liquid in the reaction vessel.

As some lead sulfate is occluded with the sulfur on the ore particles the amounts of sulfur and sulfate formed during a reaction cannot be calculated

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TP 4461D. Manuscript, Feb. 15, 1956. New York Meeting, February 1956.

Table 1. Collected Kinetic Data for Galena

Experiments Illustrate	Experiment No.	Conditions*	Initial Chlorine Concentration x 10³	Temperature, °C	Mesh	Area, Sq Cm	k	$K\Phi$ x 10⁹	p x 10⁻¹⁴
Variation of Initial Chlorine Concentration at 25°C	1	Standard 0.5 molar Cl^-, 0.1 molar H^+, pH 1.0	14.0	24.9	−10 + 14	56	0.26	1.15	9.5
	2	Standard but with 2.0 molar Cl^-	12.5	24.9	−10 + 14	56	0.31	1.15	9.5
	3	Standard	4.8	25.0	−10 + 14	56	0.295	1.15	9.5
	4	Standard	3.0	25.3	−10 + 14	56	≈0.35	1.15	9.5
	5	Standard	33.7	25.0	−10 + 14	56	0.26	Very little sulfur produced.	
			35.0	25.0			0.23		
Variation of Temperature	6	Standard	29.0	7.9	−10 + 14	56	0.10	Practically no sulfur produced.	
	7	Standard	13.0	9.5	−10 + 14	56	≈0.12	≈0.25	≈9
	1	Standard	14.0	24.9	−10 + 14	56	0.26	1.15	9.5
	8	Standard	13.0	33.0	−10 + 14	56	0.44	3.4	7.7
	9	Standard	12.8	41.0	−10 + 14	56	0.56	7.8	8.2
	10	Standard	7.0	52.5	−10 + 14	56	0.75	≈15 to 25†	≈81
Variation of Acidity	11	0.5 molar Cl^-, 0.5 molar H^+, pH 0.41	13.2	25.0	−10 + 14	56	0.27	0.67	14.3
	1	Standard 0.1 molar H^+, pH 1.0	14.0	24.9	−10 + 14	56	0.26	1.15	9.5
	12	0.5 molar Cl^-, 0.2N H^+, pH 1.7	15.5	24.8	−10 + 14	56	0.29	1.15	9.5
	13	0.5 molar Cl^-, pH 3.5	15.2	25.0	−10 + 14	56	0.21	≈1.2	≈10
Variation of Stirring Speed	14	Standard with no stirring	13.0	25.0	−10 + 14	56	≈0.02	Reaction very slow. More sulfur formed than sulfate.	
	1	Standard. Stirring at 300 rpm	14.0	24.9	−10 + 14	56	0.26	1.15	9.5
	15	Standard. Stirring at 675 rpm	13.5	25.0	−10 + 14	56	0.5 for 5 to 10 min, then 0.37	1.15	9.5
Variation of Area by Reducing Particle Size	1	Standard	14.0	24.9	−10 + 14	56	0.26	1.15	9.5
	16	Standard	14.4	25.0	−20 + 28	111	0.25	1.15	11.5
	17	Standard	13.0	25.0	−28 + 35	157	0.23	1.10	12
	18	Standard	11.9	25.0	−48 + 65	220	0.21	1.05	12.5

* In all experiments stirring rate was 300 rpm, unless otherwise stated, and initial volume was between 910 and 960 ml.
† The values of 1.15×10^{-9} and 9.5×10^{14} are the mean best values for experiment Nos. 1, 2, 3, 4, 12, and 15.
‡ Accurate data were impossible, as the rate of formation is determined by the chlorine concentration except toward the end of the experiment.

simply from a knowledge of the chlorine used up and the lead brought into solution. A soluble sulfate determination was therefore necessary and the amount of sulfur produced was assumed equal to the difference between the soluble lead and sulfate figures. The total sulfate formed, nearly always greater than the soluble sulfate, was then calculated by subtracting the *molarity* of sulfur formed from the molarity of chlorine used up and dividing the result by four. Experimental values for lead and sulfate were graphed and data for calculations read off these graphs. The reasoning behind these calculations will be clear when it is remembered that the simplest equations for the production of sulfur and sulfate from galena are

$$PbS + Cl_2 \rightarrow Pb^{++} + 2Cl^- + S$$
$$PbS + 4Cl_2 + 4H_2O \rightarrow Pb^{++} + 8Cl^- + 8H^+ + SO_4^{--}.$$

The experimental results of this work are summarized by the rate constants collected in Table I.

Microscopic examination of galena particles during reaction with chlorine showed that after 1 or 2 min the ore became covered with minute droplets of liquid which were in continuous motion on the ore surface. These droplets gradually coalesced to almost hemispherical blobs which after 5 to 10 min began to solidify, slowly depositing sulfur until a hemisphere (or sometimes a collapsed hemisphere) of sulfur remained. Typical examples of untreated and treated ores are shown in the micrographs, Figs. 2, 3, and 4. The sulfur produced in all these experiments was substantially insoluble in carbon disulfide and had a very low ill-defined melting point (95° to 100°C). An exception was the sulfur formed at 52°C, Fig. 4, which was largely soluble in carbon disulfide and had the characteristics of rhombic sulfur.

Some experiments, which will not be described here, were made with a cast slab of pile irradiated sulfur containing S^{35} to measure the rate at which dilute aqueous chlorine attacked sulfur to give sulfate. The observed rate was very small and even then mainly attributable to the action of dissolved oxygen.

Discussion

General Kinetics—For a first order heterogeneous reaction a reaction constant k may be defined by

$$\frac{-dC_{oo}}{dt} = k \cdot \frac{A}{V} \cdot C_{oo} \qquad [1]$$

where $\frac{-dC_{oo}}{dt}$ is the rate of decrease of chlorine concentration when, at a concentration of C_{oo} mole per liter, A is the area in sq cm and V the volume of the solution in CCS. As mentioned in ref. 1, the reaction of chlorine with pyrite is always transport-controlled, the reaction at the ore surface being much faster than the transport processes bringing up fresh oxidant to the surface.

A log plot of chlorine concentration against time with the data obtained with galena gave straight lines, indicating first order reactions in all instances. These plots were not as satisfactory as those obtained with pyrite, but in most cases a good straight line was obtained for up to two thirds of the reaction time and, even then, the deviation was remarkably slight considering that the ore particles became sub-

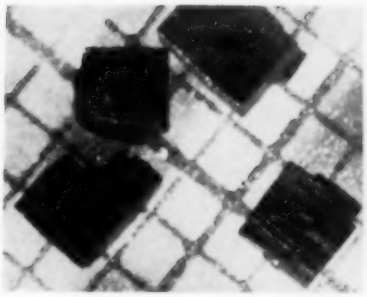

Fig. 2—Untreated galena particles. X20. Reduced approximately 50 pct for reproduction.

Fig. 3—Galena particles after reaction with chlorine water at 25°C. X30. Reduced approximately 50 pct for reproduction.

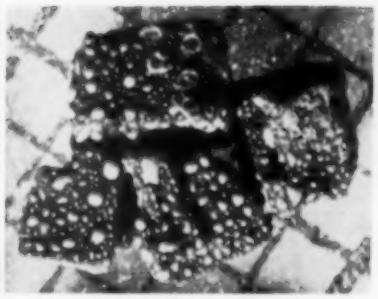

Fig. 4—Galena particles after reaction with chlorine water at 52.5°C. X20. Reduced approximately 50 pct for reproduction.

stantially covered with sulfur. Values for k, Eq. 1, are given in Table I and a few typical log plots shown in Fig. 5. It is interesting to note that the values for k do not appear to differ substantially whether the main product is sulfur, sulfate, or a mixture of the two. In view of the sulfur coating which forms during most experiments and considering that a certain degree of mutual coverage and cementation of the particles occurs during an experiment the reproducibility of k values cannot be expected to be as high as in the case with pyrite work (where particles have no tendency to stick together) and a precision of no better than about ±10 pct is claimed. The effect of particle clogging is probably responsible for the apparent steady decrease of k in the experiments where the particle size decreases, as the tendency of the sulfur coated ore particles to matte together progressively increases, thus lessening the effective surface area.

Table II. Values for Constants Used in Fig. 6

Temperature, °C	Temperature, °K	$\frac{1}{T} \times 10^3$	k, Found	k_r, from Graphical Extrapolation of k Curve at Higher Temperature	k_c, Calculated from Best Graphical Values of k and k_r
7.9	280.9	3.56	0.1	0.22	0.18
9.5	282.5	3.54	0.12	0.23	0.21
17.0	290	3.45		0.29	0.44
25.0	298	3.36	0.27	0.36	1.25
27.0	301	3.325	—	0.40	1.9
33.0	306	3.27	0.445	0.45	3.1*
41.0	314	3.185	0.56	0.56	8.3*
52.5	325.5	3.075	0.75	0.75	24*

* Not calculated directly (read from Arrhenius plot). E_r = 5000 cal, and E_c = 21,000 ±1000 cal.

Table II gives the variation of k with temperature under *standard* conditions, i.e., 300 rpm stirring, 0.5 molar Cl^-, 0.4 molar Na^+, and 0.1 molar H^+. The Arrhenius plot shown by Fig. 6 is not a straight line. This is characteristic of a reaction showing mixed chemical and transport control, a comparative rarity with reactions in solution at room temperatures. If the chemical reaction at the ore surface is sufficiently slow, a finite concentration C_s of chlorine will be present in the solution immediately adjacent to the ore surface and the rate of reaction, if first order, can be written

$$\frac{-dC_{ss}}{dt} = k_c \cdot \frac{A}{V} \cdot C_s \,. \qquad [2]$$

If it is assumed that the rate of transport of chlorine to the surface is equal to this rate, it is easily shown that k, the observed velocity constant, should be given by

$$k = \frac{k_r \times k_c}{k_r + k_c} \,. \qquad [3]$$

Since k_c increases more rapidly with temperature than does k_r, k would be expected to approach k_r at high temperature and approach k_c at low temperature. This is the case in Fig. 6, where above about 40°C the slope corresponds almost exactly to the E_r value of 4900 found with pyrite (also shown for reference on the same graph), and the k_r values for galena and pyrite are in fact as nearly equal as can be expected, considering the approximations made in assessing surface areas and the slight differences in hydrodynamic behavior between the pyrite and galena experiments. The extrapolated values for k_r at lower temperatures are also shown in Table II. From these values and the experimental results for k it is possible to calculate k_c values at different temperatures, using Eq. 3. These are given in Table II and, although of necessity approximate, the Arrhenius plot of these values in Fig. 6 will be seen to be substantially straight and correspond to an energy of activation, E_c, for the chemical reaction at the ore surface of about 21,000 cal.

As only k_r is dependent on stirring, the values for k with galena at 25°C should not be so sensitive to stirring rate as are the true k_r values found with pyrite. This is shown in Table I with stirring at 675 rpm. The b factor[1] is only 0.43 for the bulk of the reaction which is, however, a little more rapid at its commencement, when a b factor of nearly 0.8 applies. With no stirring (except to mix the solution before taking samples) a value of k corresponding to a k_r value of only about 0.02 is found.

The effects of other variables on k are also illustrated in the various sections of Table I. The pH has little effect, although at pH 3.5 a significant fraction of the chlorine is hydrolyzed to hypochlorous acid, which probably explains the somewhat low value for k. It is not clear why increasing the electrolyte concentration from the standard 0.5 molar to 2.0 molar, experiment 2, should give a significant increase in k. The initial concentration of chlorine in an experiment should have no effect on k. The quite marked increase found when a very low chlorine concentration was used, experiment 4, is discussed later.

Rate of Formation of Sulfur—A remarkable feature of the production of sulfur from galena by the reaction of chlorine is that under certain conditions the reaction is zero order with respect to chlorine.

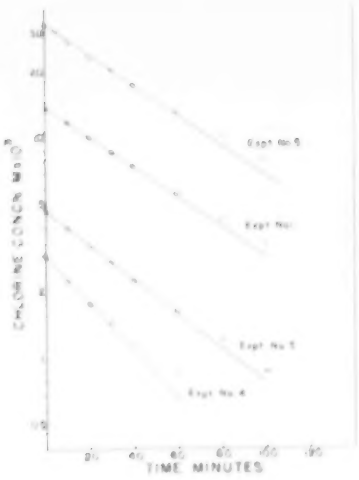

Fig. 5—Typical curves showing change of chlorine concentration with time for 56 sq cm of galena. Solutions at 25°C, stirred at 300 rpm.

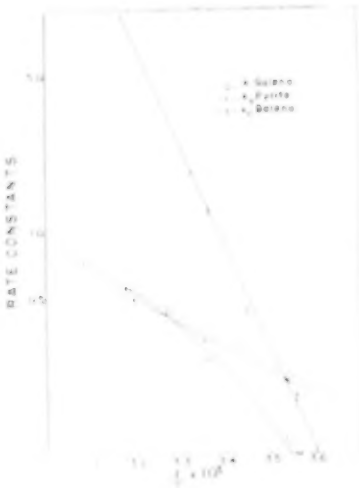

Fig. 6—Arrhenius plots for reaction of chlorine with galena.

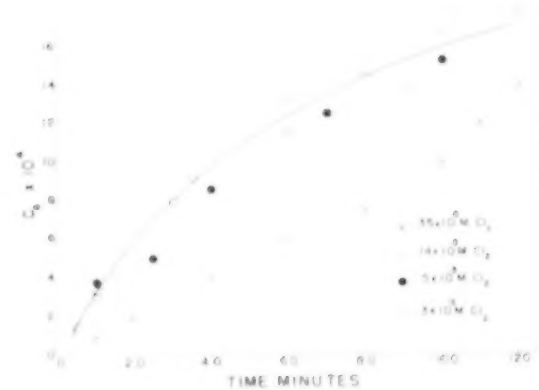

Fig. 7—Sulfur formation with various initial chlorine concentrations.

It can be seen from Fig. 7 that some sulfur concentration-time curves are substantially independent of the concentration of chlorine present. Hence, the decrease in the rate of formation of sulfur with time is not caused primarily by chlorine concentration changes, but by some effect arising from the presence of sulfur itself. For corrosion reactions, giving rise to adherent solid products, three rate laws are commonly encountered; a linear law when the product is porous, a parabolic law arising from diffusion through a layer of reaction product, and an exponential law derived by Evans[5] on the basis of a Poisson function for the blocking of reaction *channels* through an otherwise impervious film of reaction product.

The *self stifling* exponential law gives about the best overall prediction of the present results for sulfur formation on galena. The mechanism, however, cannot be the same as that operative with corrosion through oxide films, since even when the rate of sulfur formation has decreased to practically zero the ore surface continues to react with chlorine at a rate which is only slightly reduced from its initial value. It must be concluded, therefore, that although all the galena surface (or the coating on the ore proper) can react with chlorine, only a comparatively small fraction, or only a certain number of reactive sites, can give rise to sulfur formation, and that the sulfur thus produced blocks or in some way inhibits the subsequent reaction of these sites.

A self stifling exponential equation may be written

$$\frac{dN_s}{dt} = K A \exp\left(\frac{-pN_s}{A}\right) \qquad [4]$$

where N_s is the number of moles of sulfur formed; K, a rate constant in moles, cm^{-2} min^{-1}; and p, which has the units of cm^2 $mole^{-1}$, is such that $p \cdot \frac{dN_s}{A}$ is the mean frequency of blocking or inhibiting of reactive sites by each incremental increase of sulfur, $\frac{dN_s}{A}$ mole per unit area.

Eq. 4 on integration gives

$$N_s = \frac{2.3\,A}{p} \log (K\,p\,t + 1) \cdot \qquad [5]$$

For convenience, as data have been expressed with the fictitious *concentration* of sulfur, C_s, a derived form of Eq. 5 can be plotted

$$C_s = \frac{2.3}{p'} \log \left(K' \frac{A}{V} p' t + 1\right) \qquad [6]$$

the integrated form of

$$\frac{dC_s}{dt} = K' \frac{A}{V} \exp\left(-p'C_s\right) \qquad [7]$$

where K' equals $1000K$, and p' is a constant at a given area and equal to $\frac{p\,V}{1000A}$. Plots of Eq. 6 are shown in Fig. 8. Agreement between a mean line and experimental values at room temperature is fair considering the likely experimental errors, although values for C_s in the first 30 min are appreciably lower than the equation predicts. The agreement is excellent at higher temperatures and with greater

surface areas of ore and there is little doubt but that Eq. 6 represents the observed values with some precision, certainly better than any other equation tried.

Values for K and p are given in Table I for all experiments where appreciable quantities of sulfur were formed. The p varies a little from experiment to experiment, but is substantially constant at 10^5. No doubt the differences, such as a decrease with rise in temperature and an increase with decrease in particle size, depend on uncontrolled factors such as the mutual coverage and packing of ore particles in the apparatus. K is markedly temperature dependent, however, and gives the Arrhenius plot shown in Fig. 9, which is a straight line corresponding to an activation energy of 22,000 cal.

Between pH 1 and 3.5, p and K are constant at 25°C. At pH 0.4 (a solution of 0.5N hydrochloric acid), there is a marked decrease in K and increase in p but these conditions are extreme and the logarithmic law may no longer apply. As would be expected from a reaction independent of the chlorine concentration, changing the stirring speed from 300 to 675 rpm had no significant effect on K or p. Eq. 5 predicts that the sulfur formed in a given time should be directly proportional to the surface area A. This is found to be approximately the case in experiments 1, 16, 17, and 18. It is illustrated by Fig. 10, where the area increases fourfold due to a decrease in particle size. This leads to the interesting conclusion that the yield of sulfur resulting from the consumption of a given amount of chlorine can be greatly increased simply by decreasing the particle size or by increasing the number of particles of ore present in the chlorine solution, a most unexpected result.

Although sulfur formation is roughly zero order with respect to chlorine at concentrations between about 3×10^{-4} molar and 15×10^{-4} molar, with chlorine concentrations of about 25×10^{-4} molar or greater there is a marked decrease in the amount of sulfur formed, as will be seen in Fig. 7. At low temperature with high chlorine concentration only sulfate is produced with traces of sulfur. The sulfur production must, however, be dependent on chlorine concentration when the rate of formation of sulfur, as predicted by Eq. 4, requires more chlorine than can be brought to the galena surface by transport (Eq. 1, when $k = k_t$). This can occur under conditions of high temperature unless the chlorine concentration is suitably increased, and at very low stirring speed. In the borderline condition of experiment 4, Table I, where the chlorine concentration is very low, the value for k apparently increases to a figure corresponding to the k_t value at that temperature in an endeavor to provide enough chlorine for the sulfur reaction to take place at the normal speed. This can only occur because the reaction of chlorine at 25°C is not completely transport-controlled and an appreciable concentration, C_s, of chlorine is found at the ore surface.

Rate of Formation of Sulfate—In all experiments, except those at very high chlorine concentration, the kinetics are dominated by the rate of formation of sulfur, even to the extent, as seen in experiment 4, of apparently increasing the rate constant k for the reaction of chlorine if this can help to maintain $\frac{dN_s}{dt}$ at its correct value. Generally speaking, therefore, sulfate appears at a rate equal to the difference be-

Fig. 8—Plot of Eq. 6 for sulfur formation at various temperatures.

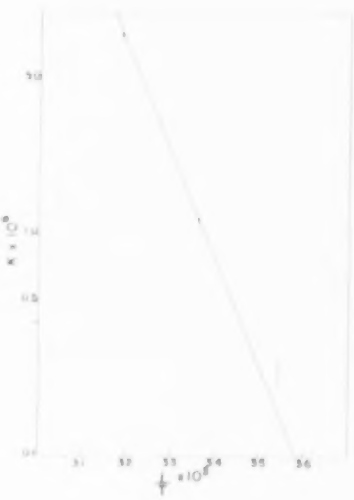

Fig. 9—Arrhenius plot for formation of sulfur on galena.

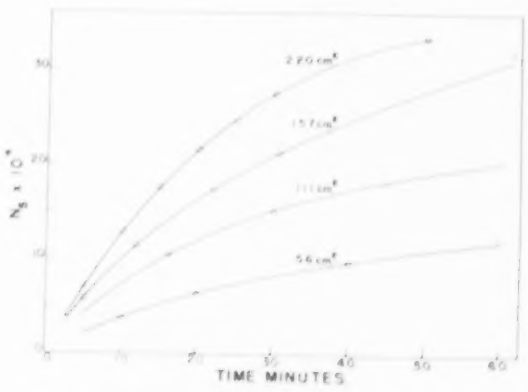

Fig. 10—Formation of sulfur from various areas of galena surface.

tween the rate of formation of sulfur and one quarter the rate at which chlorine is consumed.

Experiments with radioactive sulfur showed that the amount of sulfate produced by the direct action of chlorine on sulfur element is very small, k having a value of only about $2 \cdot 10^{-5}$ compared with 0.2 for the sulfide ore at room temperature.

In the two experiments in which chlorine could not react fast enough to produce all the sulfur potentially capable of being formed there was, nevertheless, some sulfate produced. This, it is supposed, arose in large measure from the fact that elementary sulfur is formed initially via sulfur chloride which can transform, at most, 75 pct

$$4S\,(I) \rightarrow 3S + S\,(IV)$$

or 83 pct

$$6S\,(I) \rightarrow 5S + S\,(VI)$$

of its sulfur content to the element, the rest being hydrolyzed and oxidized to sulfate. In both experiments 4 and 10 the ratio of S(O) to S(VI) is 5:1 throughout the duration of the experiments and 80 to 85 pct S probably represents the maximum yield of the element which is possible. By working at low temperature and high chlorine concentration, however, a 100 pct yield of sulfate should be feasible.

The calculations made to assess the quantities of sulfate formed in all these experiments were made assuming that only sulfur and sulfate are produced. The production of sulfur chloride does not affect the sulfur curves which are the same irrespective of whether the product is sulfur or sulfur chloride because they represent insoluble sulfur associated with soluble lead. However, if only sulfur chloride is formed the true sulfate curves will be a little lower than shown. As the coating on galena gradually changes from sulfur chloride to sulfur at a rate not precisely known, the exact sulfate curves cannot be calculated and they have been reported as if sulfur were the only insoluble form of the element. The errors are not very great, especially near the end of each experiment.

Reaction Mechanism—The rate constants found in this investigation can be summarized by the expressions

$$k_c = 4 \cdot 10^{-7} \exp\left(\frac{-21{,}000}{RT}\right)$$

$$k = 3.5 \cdot 10^{7} \exp\left(\frac{-21{,}000}{RT}\right)$$

and

$$k_t = k_t' \exp\left(\frac{-4900}{RT}\right)$$

with k being given in terms of k_c and k_t by Eq. 3. The value of k_t' depends on the stirring rate and exact apparatus used, being about $1.45 \cdot 10^{5}$ for the present work.

It will be seen that, for the maximum production of sulfur, both a high temperature and small particle size are desirable, the former being limited in practice to about 60°C because of the solubility of chlorine. At elevated temperatures the overall reaction may be largely transport-controlled. Hence, vigorous agitation will be advantageous. The maximum chlorine concentration that can be tolerated at elevated temperatures before a breakdown in sulfur formation occurs is not known exactly but for safety should be restricted to below about 0.05N. If only sulfate is required as an end product, however, the chlorine concentration level should be maintained at 0.05N or greater with as low a temperature as is practicable.

It would be unwise to postulate with any certainty at this stage the mechanism of the reactions taking place before a study of the behavior of other ores has been completed. The reaction has several points of interest, however, which are worth discussing.

The reaction is very fast with pyrite and neither sulfur nor sulfur chlorides is formed at any stage. The reaction with galena, on the other hand, is much slower and some chemical control is observed at room temperature. Most, if not all, of the sulfur produced originates from the initial formation of a liquid which can scarcely be other than a sulfur chloride, presumably monochloride, as a similar liquid is seen when bromine is used and SBr_2 does not exist. This liquid is seen with other ores, such as sphalerite and chalcopyrite, which also oxidize to give sulfur.

The presence of sulfate as a product in the galena reaction can arise from a series of fast reactions involving a SCl_3 transition complex, chlorine molecules, water, and S_2Cl_2, which hydrolyzes to give elementary sulfur in some 75 to 85 pct yield. The mechanism of this hydrolysis has been the subject of much controversy in the literature and its nature is not yet settled.[11] It is known to give rise to a form of sulfur insoluble in organic solvents and of low melting point,[9] such as is found in this work.

The sulfur formed dissolves in the remaining sulfur chloride and can be seen to precipitate out as the reaction proceeds. If this hydrolysis did not take place the monochloride would eventually be oxidized by chlorine. The formation of globules of S_2Cl_2 on the galena surface, which always occurs when solutions are stirred at an appreciable rate, protects the monochloride to some extent. However, when the surface layer concentration of chlorine becomes too great, the direct attack of S_2Cl_2 by chlorine becomes comparable with the hydrolysis rate and the rate of formation of SCl_2 and an overall loss of sulfur chloride occurs before globules can form. The production of sulfur is then erratic and very low.

Matters are further complicated by the fact that both chlorine and sulfur are freely soluble in sulfur chlorides. However, chlorine dissolved in either sulfur monochloride or dichloride does not attack galena to any appreciable extent. The presence of water as a third phase may, however, modify the picture. This matter will be further studied.

Acknowledgment

This work was carried out under Grant No. 9535 of Project D.44-95-35-05 from the Defence Research Board of Canada, and acknowledgment is gladly made to the Board for permission to publish.

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Discussion of this paper sent (2 copies) to AIME by Aug. 1, 1957 will appear in AIME *Transactions* Vol. 212, 1958, and in JOURNAL OF METALS, October 1958.

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AIME NEWS

A Salute to AIME'S "Mr. Transactions"

Ezra J. Kennedy, Jr., Retires

One of the best known members of AIME stepped down from full-time activity on May 1. Mr. Ezra J. Kennedy, Jr.'s retirement was marked by many expressions of appreciation for his 30 years of service to the Institute from AIME officers and members whom he counts among his host of friends. Numerous resolutions to this effect were passed at business sessions of committees during the Annual Meeting, and at informal gatherings of individual members. At the joint meeting of the AIME Executive and Finance Committees on April 15, a resolution honoring Mr. Kennedy was unanimously voted. (See text of resolution below).

These sentiments, showing the affectionate regard in which Mr. Kennedy is held, were also echoed at the luncheon in his honor on April 30, at the Brass Rail Restaurant in New York, attended by the entire AIME staff. Each department head rose to publicly thank Mr. Kennedy for his courtesy, patience, and generous assistance. These qualities also proved invaluable to the thousands of authors with whom he worked closely, all of whom found his innate tact bespoke a true gentleman of the old school.

Associated with the Institute since 1925, Mr. Kennedy has been successively Assistant to the Secretary, and since 1944, an Assistant Secretary. During these years he devoted his efforts primarily to the technical publications, working on every volume of *Transactions* from 1925 to 1949. To members of the Institute he was *Mr. Transactions*. In addition to *Transactions* he handled at least part of the job on most of AIME's books issued during these years, guiding committees in maintaining a high standard of quality. He also found time for many of the details of Annual Meeting organization, and set up the programs for publication.

Ezra J. Kennedy, Jr., is a native of Detroit where he was born on Apr. 1, 1887, to Ezra, Sr., and Nellie Kennedy. A graduate of the University of Michigan, he married Helene L. Euler, who passed away in 1944. Since 1949 he has been happily married to the former Madeline D. Beekman.

After working as a chemist for Charles F. Pfizer & Co. and later with the Air Reduction Co., "E. J." accepted a position as market reporter on the staff of the New York *Journal of Commerce*. This led to the post of associate editor on the *Oil Trade Journal*. In 1921 he joined the publicity and statistics department, American Petroleum Institute,

leaving to begin his long and happy association with AIME.

Although Mr. Kennedy will be editor and handle the publication of various conference *Proceedings*, he will have the opportunity for more time for his favorite hobby. The Kennedys find driving their car through the countryside and enjoying the changing landscapes, the most satisfactory form of relaxation. Everyone at AIME wishes them happy motoring under fair skies.

Resolution in Honor of

EZRA J. KENNEDY, JR.

WHEREAS, the Board of Directors of the American Institute of Mining, Metallurgical, and Petroleum Engineers takes note that Assistant Secretary EZRA J. KENNEDY, JR., will retire April 30th, 1957, after thirty-one years of devoted service;

RESOLVED, that the Board of Directors commends Ezra J. Kennedy, Jr., for his faithful, unassuming performance as secretary of the Institute Technical Publications Committee; and that the Board of Directors particularly recognizes his success in maintaining the high quality of the Institute's *Transactions* while winning the respect and friendship of thousands of authors.

April 15, 1957 — GROVER J. HOLT, President

R. C. Cole Serves As EMD Vice Chairman

R. C. Cole was nominated as vice chairman of the EMD for a one-year term beginning Mar. 1, 1957, replacing H. H. Kellogg, who will serve as chairman-elect during 1957. W. R. Opie was nominated for a three-year term as vice chairman of the division.

IMD Committee Plans Program for Chicago

The IMD Metal Science Committee has arranged two sessions of invited talks for the Chicago meeting, November 4 to 7. One Monday morning will be devoted to *Structure of Solid Solutions*, and Tuesday morning the subject will be *Science of Alloy Hardening*. Three or four outstanding men will contribute related talks to each of these sessions, and discussion from the floor will be encouraged. Two sessions of contributed talks are scheduled for the afternoons, each on the same general subject matter as the corresponding morning meeting.

The Committee wishes to encourage the IMD membership to submit abstracts related to these topics according to the new procedure described in the *Editorial*, JOURNAL OF METALS, May 1957, page 651. (Send three copies of abstracts, 200 to 300 words, to IMD Programs Committee, Metallurgical Society of AIME, 29 W. 39th St., New York 18, N. Y.) Insofar as possible, these contributions —which are intended to be similar in timeliness, interest, and brevity to the *Research in Progress* talks of the past few years—will be scheduled for the appropriate Metal Science session.

Abstracts for the contributed session on *Structure of Solid Solutions* could be concerned with X-ray evidence for clustering and order in solutions, magnetic resonance studies of alloys, substitutional vs interstitial solubility of impurities in semiconductors, theory of solid solutions, thermodynamic studies, influence of irradiation on solution properties, and other related topics. Those for the session on *Science of Alloy Hardening* could treat the strength of solid solutions, precipitation hardening, dislocation theory, mechanical effects of order and of clustering, and other topics in this general area.

In summation, two sessions of invited talks are scheduled for the mornings and two sessions of contributed talks are scheduled for the afternoons. The Committee wishes to encourage the submission of abstracts for the contributed sessions, and also to encourage attendance at all four sessions.

Coed Wins Engineering Scholarship at Michigan

An 18-year-old coed, Nancy LaTendresse, is the first girl to win an industrial scholarship in the University of Michigan College of Engineering.

The award is given by International Nickel Co. Inc. for studies in metallurgical engineering and includes $500 a year for four years to the winner, in addition to $500 annually to the University.

Toastmaster D. R. Loughrey addresses the Fellowship Dinner. Seated at the head table are, left to right, President Holt and Major General Medaris.

Pittsburgh Steelmaking Conference Breaks All Attendance Records

Breaking attendance records is nothing new for the Blast Furnace, Coke Oven, and Raw Materials Conference and the National Open Hearth Steel Conference. This year at the 40th annual meeting they did it again with a combined registration of 1858 at the Penn-Sheraton Hotel in Pittsburgh.

The registrants came to hear some 50 technical papers. One session was on ore agglomeration where a paper was given on the updraft pellet hardening technique practiced by Cleveland-Cliffs. E. W. Voice, noted sintering research specialist of the British Iron & Steel Research Assn., presented a paper reviewing experiments on the theory of sintering. At a later session, he gave detailed observations of Russian blast furnace techniques acquired during his recent trip.

M. O. Holowaty and C. M. Squarcy of Inland Steel presented the JOURNAL OF METALS Award paper, *High-Temperature Testing of Blast Furnace Coke*. On the open hearth side, Keith Moore of Steel Co. of Canada told of the results and problems developing from high firing rates practiced at Steelco. With this as background, an entire afternoon was given to a series of progress reports on all-basic open hearth construction. And these were but a few

The Social Hour provided an opportunity for an exchange of ideas. Left to right, President Holt, Major General Medaris, Leo F. Reinartz, a Past President of AIME, D. R. Loughrey, W. D. Smith, and C. T. Marshall

NOHC Chairman D. R. Mathews left, is shown presenting the Frank B. McKune Award to W. D. Smith, for his paper *Manufacture of Leaded Steels*.

highlights of the conference.

At the Annual Luncheon and Business Meeting of the Blast Furnace, Coke Oven, and Raw Materials Committee, chairman C. T. Marshall presided. A. W. Thornton, past-chairman of the Metals Branch Council, explained the workings of the new Metallurgical Society of AIME, while AIME President Grover J. Holt gave his best wishes to the Committee. The following officers were unanimously elected for 1956: F. M. Hamilton, Chairman; R. E. Powers, Vice Chairman; R. L. Stephenson, Vice Chairman; and E. K. Miller, Jr., member of the Executive Board.

Weirton Steel Co.'s male chorus provided music at the Fellowship Dinner. National Open Hearth Chairman D. R. Mathews presented the Frank B. McKune award to W. D. Smith of Jones & Laughlin for his paper, *Manufacture of Leaded Steels*. The Conference Award paper, *Factors Affecting Heat Time*, was written by T. A. Cleary, Jr., of Youngstown Sheet & Tube Co. Toastmaster of the evening was D. R. Loughrey, who presented the guest speaker, Major General John B. Medaris, Chief of Army Ballistics, Missiles Agency, Redstone Arsenal, Ala. General Medaris, who spoke on *The Missile Age*, stated, "Seldom have men been able to stand on the doorstep of a new age and recognize that it was, in truth, the dawning of a new era." He continued, "The Army's success in the development of guided missiles has produced, and will continue to produce, many dividends for industry and the consumer in many fields. The advent of the Missile Age and the union of atomic fission with missile guidance will provide man with a means to explore the universe and lead him eventually into the Age of Space. The prudent use of natural forces now available to mankind demands an increase in moral and ethical stature commensurate with the progress of science and technology."

On the last day, conference members were guests of Weirton Steel Co. at their Weirton, W. Va., plant. A special train transported almost 500 persons from downtown Pittsburgh into the plant grounds where a fleet of buses was waiting to move out in four groups to various points in the plant. The tour was handled with fantastic precision; while some 100 persons were guided through the new 56-in. continuous hot strip mill, another group inspected one of the plant's 1200 tpd blast furnaces, and a third group observed the tin mill's continuous lines turn out an endless ribbon of plate. The vast multitude was served a buffet luncheon at the beautiful million-dollar Weirton Community Center. But the chief source of interest, particularly for the open hearth men, was Weirton's gigantic open hearth shop, the largest in the world. There could be seen the new 600-ton furnace, two 550-ton furnaces, one 500-ton furnace, and ten other large open hearths.

At the close of the three-day meeting, everyone agreed that they had enjoyed themselves and learned a great deal too.

Between sessions, Chairman of the Blast Furnace Committee C. T. Marshall, left, chats with AIME President Grover J. Holt, center, and NOHC Chairman D. R. Mathews.

Featured speaker at the Fellowship Dinner was Major General John B. Medaris, who addressed the guests on the subject of *The Missile Age*.

Seated at the Speakers' Table during the Banquet in the Carter Hotel, Cleveland were, left to right: R. W. Shearman, M. A. Steinberg, A. D. Schwope, Willy Ley, R. F. Hehemann, G. M. Ault, W. R. Hibbard, Jr., W. A. Dean, and W. A. Johnson.

New Committee Sponsors Successful Conference Devoted To High-Temperature Materials in Cleveland

Six-hundred fifty engineers and scientists in the specialized field of high-temperature materials gathered at the Carter Hotel in Cleveland on April 16 to 17 for a special meeting held by the newly formed High-Temperature Alloys Committee of the Institute of Metals Division. Registration for the meeting surpassed the highest expectations of the Conference Committee, and, what is especially important, the meeting was truly national in character, with scientists from Massachusetts to California in attendance.

Sessions were held on the subjects of cobalt and nickel-base alloys, cermets, intermetallics, refractory metals, vacuum melting, environmental studies, gas-metal systems, and oxidation. Highlight of the two-day meeting was the speech of Willy Ley, noted author and authority on missiles and space flight. His talk, *The Conquest of Nearby Space*, dealt with Project Vanguard and what could, or should, come after it. Mr. Ley is in the position of being very well informed on the subject, but not limited in what he can say by security restrictions. The banquet, at which Mr. Ley spoke, was attended by 350.

G. M. Ault headed the Conference Committee, and his group worked closely with the ever-hospitable Cleveland Local Section, under the chairmanship of R. F. Hehemann. N. J. Grant is Chairman of the IMD High-Temperature Alloys Committee, which sponsored the meeting.

A feature of the technical sessions was the presentation of a survey paper in each field, specially prepared for the meeting, which gave a summary of the present status and future prospects of each topic under discussion. Several of these papers will appear in the July issue of JOURNAL OF METALS. It is also expected that some of the technical papers will appear in JOURNAL OF METALS *Transactions*.

As the first meeting sponsored by the High-Temperature Materials group, a pace has been set that will be hard to match in the future.

Chatting with guest speaker Willy Ley, center, are Morris Steinberg, Program Committee, left, and W. R. Hibbard, Jr., Vice President, Metallurgical Society of AIME.

Willy Ley's stimulating talk provoked much interest. He is seen here, center, in animated discussion with O. T. Marzke, left, co-chairman of the High Temperature Properties Session, and R. F. Hehemann, Cleveland Section Chairman.

NOHC Ohio Section Holds Annual Meeting

The Northern Ohio Section of the National Open Hearth Steel Committee held its annual meeting at the Pick-Ohio Hotel, Youngstown, Thursday, March 7. The technical session featured papers on *Open Hearth Pit Pouring Practice* presented by F. J. Herman, U. S. Steel Corp., Youngstown. A film on safety in the steel plant was shown by Walter T. McLean, also of U. S. Steel. The third paper dealing with *Factors Affecting Heat Time* was offered by T. A. Cleary, Jr., Brier Hill Works, Youngstown Sheet & Tube Co. This was followed by a training film on electric furnace operations presented by J. A. Brasonic, Electrical Laboratory, Republic Steel Corp., Cleveland, with comments by A. K. Blough of Republic Steel in Canton, Ohio. Concluding the technical session was a paper on *The Oxygen Converter Process* by Joseph K. Stone, Jr., Steel Plants Div., Kaiser Engineering, Oakland, Calif. Co-chairmen of the technical session were K. F. Waggener, Republic Steel Corp., Youngstown, and E. Britt, Youngstown Sheet & Tube Co.

At the Fellowship Dinner, the group was addressed by John D. Grewell, industrial relations staff supervisor for Westinghouse Electric Corp. in Sharon, Pa. E. J. Brandon, of U. S. Steel in Youngstown, served as toastmaster.

The Northern Ohio Section of the NOHC is under the leadership of Joseph Turner, and J. F. Beale is secretary of the group. Both men are associated with Republic Steel in Youngstown.

Additional Scholarships Offered by Atlas Powder

Atlas Powder Co. will add two Merit Scholarships to the company's college student assistance program now in its fourth year. Winners will be selected by the National Merit Scholarship Corp. which conducted competitive exams last fall in high schools throughout the country. Those who scored the highest grades were chosen for the company's scholarship and for others given by cooperating sponsors.

Six colleges will also receive direct grants of $1000 each, to be awarded to one or two senior students in chemistry, physics, or engineering at each of the schools. The colleges selected are: University of Missouri School of Mines & Metallurgy, Michigan College of Mining & Technology, Colorado School of Mines, Drexel Institute of Technology, Lehigh University, and Lafayette College.

Scholarship winners are also offered practical experience through summer work in one of Atlas' 11 plants or 3 research laboratories.

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After a smooth flight to Portland, AIME President-Elect Augustus B. Kinzel, center, chats with Field Secretary Roy E. O'Brien, left, and Don W. Johnson, general chairman of the conference.

Pacific Northwest Regional Conference Scores With Superior Technical Sessions, Outstanding Speakers, Interesting Field Trips

The staff of the USBM Experimental Station in Albany, Ore., is shown welcoming conference visitors on their arrival from Portland for an all-day tour of the activities at the Bureau Station, the Oregon Metallurgical Corp., and the Wah Chang Corp.

A bevy of top-flight engineers including President-Elect Augustus B. Kinzel, convened in Portland, Ore., April 11 to 13 for AIME's three-day Pacific Northwest Regional Conference. More than 200 persons representing Oregon, Washington, Idaho, Wyoming, Montana, British Colombia, and Northern California, signed the registration book at the Multnomah Hotel. Included in the group were about 30 wives.

On the opening day, Thursday, delegates chose between two tours. One was to the Oregon Metallurgical Corp., the Wah Chang Corp., and the USBM at Albany, Ore., with a luncheon stopover in Corvalis, where the guest speaker was W. J. Kroll, metallurgical consultant.

The alternate Thursday tour was to Portland's new multi-million dollar glass container operation, the Owens-Illinois Glass plant.

Relaxing between sessions in the Multnomah Hotel are George Beard, left, guest speaker at the Friday luncheon and R. R. McNaughton, who gave the keynote address on Saturday.

In this scene taken at the banquet on Friday, President-Elect Augustus B. Kinzel is shown addressing the guests. Seated left to right: D. W. Johnson, R. E. O'Brien, and T. E. Kesler.

On the tour of USBM Experimental Station in Albany, Ore., Charles C. Nolan stops to examine the display of a valve fabricated from titanium metal.

Two outstanding luncheon speakers were heard Friday and Saturday. George Beard, assistant vice president, Pacific Power & Light Co., addressed the luncheon guests on Friday. His topic was *Possible Effect of Coal Utilization on Northwest Power Production*.

Speaker for the Saturday luncheon was R. R. McNaughton, metallurgical manager for Consolidated Mining & Smelting in Trail, B. C.

Dr. Kinzel, the featured speaker at the Friday night banquet, discussed *Research and the New Metallurgy*. He has lectured throughout the world.

Two days of the conference were devoted to technical sessions covering geology, extractive metallurgy, industrial minerals, iron and steel, minerals beneficiation and physical metallurgy.

Among the outstanding papers presented were: *Riddle Nickel Deposit* by W. A. Foster, Hannah Coal & Ore Corp.; *Chemical Requirements of the Western Mineral Processing Industry* by Raymond E. Byler of Arthur D. Little Inc.; *Alloys 5086 and 5083* by M. C. Fetzer, Kaiser Aluminum and Chemical Corp.; *Streaming Potential in Flotation* by D. W. McGlashan, Montana School of Mines. Professor McGlashan gave a second outstanding paper, *Rheological Consideration of Manganese Oxide Ores*.

During the conference the ladies were entertained with a morning coffee hour, and a luncheon and fashion show in the Rose Bowl.

Much of the success of this conference can be attributed to the work of the following: Donald W. Johnson, general chairman; technical sessions chairmen, Hollis Dole and Fay Libbey, Geology; Pierre Hines and Emmons Coleman, MBD; Ralph Mason and Chester Kershaw, IndMD; and John Anderson, Francis Cappa, Vincent Belusko, Donald Ingvolstad, Haruo Kato, Metals; Edward Vistica, general arrangements chairman; and John Yeasley, field trips.

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AROUND THE SECTIONS

George B. Harrington, left, is seen receiving the 50-year certificate and medal of the Legion of Honor from Michael Tennenbaum, chairman of the Chicago Section.

• When the **Chicago Section** met on April 3 at the Chicago Bar Assn., the featured speaker was F. G. Jaicks, assistant general manager, Inland Steel Co. who addressed the group on the subject of *Recent Experiments in Continuous Casting of Steel*.

George B. Harrington received the 50-year certificate and medal of the Legion of Honor. The presentation was made by chairman, Michael Tennenbaum. Mr. Harrington was the recipient of the William Lawrence Saunders Gold Medal in 1944.

• The Annual Meeting of the **Colorado Plateau Section** was held on Saturday, March 9, in Grand Junction. The technical sessions and business meetings took place in the Civic Auditorium while the La Court Hotel was the scene of the cocktail party, dinner and informal dance in the evening.

The technical program was varied and consisted of a paper, *Slurry Pipeline as an Integral Link in Gilsonite Refining Project*, by Lee Morris and John Henderson. This was followed by a movie and discussion on Continental Uranium Co.'s Open Pit Operations by John Rosco and Herb Reynolds. Concluding the program was a sound film *Mining For Nickel*, which describes Inco's Canadian operations.

• The **Montana Section** met on March 20 in the Montana School of Mines in Butte. Featured speaker was John G. McCaslin, assistant professor of physics at the school who discussed *Instrumentation in the Mineral Industry*. The Section also attended a showing of the film, *Hemo the Magnificent* on March 25 at the Museum Hall of the school.

• The **St. Louis Section** meeting on March 8, was held on the campus of the Missouri School of Mines & Metallurgy, Rolla, Mo. The school and the USBM held open house.

Featured speaker at the dinner was F. Rolf Morral, Battelle Memorial Institute, who addressed the Section on the subject of *The Production and Uses of Cobalt*. Dr. Morral illustrated his talk with a sound film in color, *Cobalt in Katanga*. Members of the WAAIME also attended the dinner and evening program.

• The **Western Section** Steel Group held a dinner meeting on March 13 at the Rodger Young Auditorium in Los Angeles. Theme of the program was refractories, and a film was presented showing how clay, silica, and basic refractories are produced.

• The **Pittsburgh Section** met on April 18 at the Westinghouse Research Laboratory Auditorium. Guest speaker for the occasion was J. K. Stanley, Crucible Steel Co. of America, who discussed *Decarburization Phenomena in Carbon, Alloy and Silica Steels*.

• The **Connecticut Section** held its technical session and annual meeting on March 26, at the Chase Country Club in Wolcott, Conn. After dinner, guests heard a talk by E. G. Vogt, manager of INDUCTOVAC Pilot Plant, Universal-Cyclops Steel Corp., Bridgeport, Pa. Dr. Vogt's topic was *Vacuum Metallurgy—Art or Science?* He discussed improvements possible through vacuum melting, such as increased fatigue strength at high temperatures and excellent low temperature properties. He then offered some theories to explain the results attained. Dr. Vogt also analyzed the chemistry and thermodynamics of gas removal from a molten metal, relating some of the factors and problems to pumping systems in commercial vacuum melting installation. Prior to the technical session, the Section held a short business meeting at which time the report of the nominating committee was read.

• The **San Francisco Section** held a dinner-dance with the Ladies' Auxiliary in the Terrace Room of the Fairmont Hotel on March 23. Entertainment chairman Fred Lohse engaged Rod McCauley's orchestra and other top flight entertainers who provided a good time for members and guests.

On the Move, **a new 16-mm color sound film, which runs 28 min, is now ready for showing. The film deals with the subject of transportation and points out the important role played by road building equipment. The St. Lawrence Seaway project, material handling, and general turnpike construction are covered. The human interest plot offers the story of a student engineer who is confronted with a career decision. A limited number of copies are available from the producers, Baldwin-Lima-Hamilton Corp., Advertising Dept., Lima, Ohio.**

A film entitled *News From the Coal Country* **is available for free loan distribution from Modern Talking Picture Service Inc., 3 E. 54th St., New York 22, N. Y. Produced by the North American Coal Corp., the film can be obtained only in the following states: Illinois, Michigan, Minnesota, New York, North Carolina, Ohio, Virginia, West Virginia, and Wisconsin.**

Research—Key to Progress **is a 16-mm sound, color film available free from the Public Relations Dept., Armour Research Foundation, 10 W. 35th St., Chicago, Ill. The documentary film which runs 15 min, depicts the role of industrial research in the nation's economy, tracing the phenomenal rise of research and its contributions to the high standard of living in the U. S. It was produced by Armour as a public service.**

Zinc Controls Corrosion **is a new 16-mm sound color film of 38-min duration, available free, except for shipping costs, from Rothacker Inc., 729 Seventh Ave., New York 19, N. Y. Produced by the American Zinc Institute, the film explains the basic cause of corrosion, zinc coating methods to protect steel, and a review of fabricating articles from galvanized sheet and strip. Some spectacular examples of corrosion protection with zinc are pictured: a giant TV tower, the Brooklyn Bridge, and the new atomic submarine Sea Wolf. State alternate choices of playing dates.**

Regional Steel Meeting Successful in Detroit

The AIME Regional Meeting on Deep Drawing Steels held in Detroit, March 18-19, attracted an unusually large attendance of about 400 registrants. Sponsored jointly by the Detroit Sections of AIME and of the National Open Hearth Steel Committee, this unique conference devoted the first day to papers on the process metallurgy of deep drawing steels and the second day to their physical metallurgy. In all, 12 technical papers were presented by eminent authorities on sheet steel.

Significantly, this regional meeting took place in Detroit, the center of the auto industry in America. Many of the authors, and a majority of the audience were from the auto manufacturers or from steel companies supplying steel for auto bodies.

Under discussion at the process metallurgy sessions were such subjects as chemically capped steel, mechanically capped steel, deep drawing rimmed steel, aluminum killed steel, and hot mill practice.

At the sessions on physical metallurgy these topics were covered: behavior of carbon and nitrogen, strain aging, vanadium-treated drawing steels, elements affecting drawing properties, physical properties influencing deep drawing behavior, appreciation and testing of body sheet, and selection and processing of sheet steel for auto body panels.

Technical meetings were held in the spacious facilities of the Rackham Building, at the Engineering Society of Detroit. However, the *S.R.O.* sign was out during the Monday sessions with every seat in the auditorium occupied.

A bound volume of the Conference Proceedings containing the technical papers presented will be sent later to all registered AIME members and will also be available for sale to others.

A fellowship dinner was held on Monday evening, March 18, with 320 present. Donald N. Frey, general chairman, presided as toastmaster. Speaker of the evening was J. Lance Rumble, General Motors Corp. of Canada. His address, *Back Talk From the Rumble Seat*, was interspersed with humor and philosophy.

The AIME Detroit Section is under the chairmanship of J. H. Olson, Engineering Div., Chrysler Corp. Robert E. Mahr, Missile Operation of Chrysler is secretary; and Bryan Beckwith, Commonwealth Industries, is treasurer. Detroit NOHC officers are: chairman, M. Groat, Great Lakes Steel Corp., and secretary, Harry W. Clark, Ford Motor Co.

Others who deserve credit for planning and executing the successful two-day meeting are: Donald N. Frey, Ford Motor Co., general chairman; Kenneth B. Valentine,

(Continued on page 810)

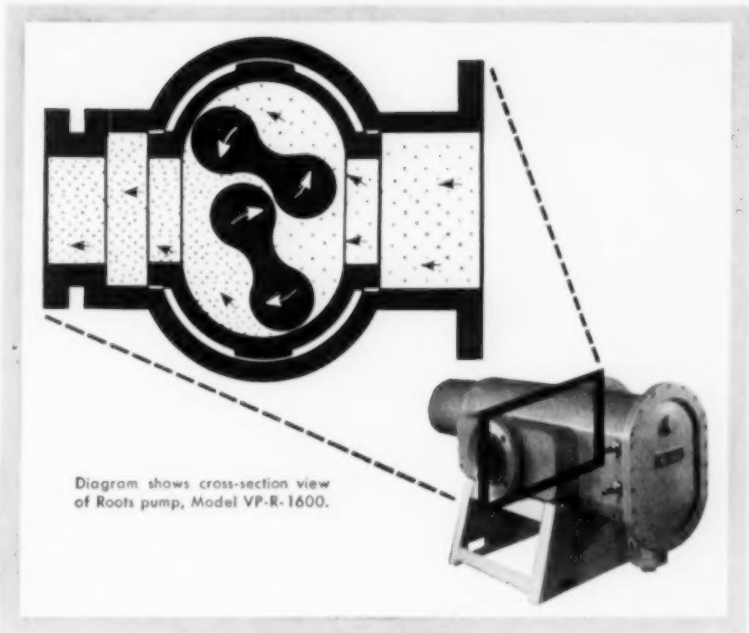


Diagram shows cross-section view of Roots pump, Model VP-R-1600.

How to get vapor-free high vacuum

fast . . . with the ROOTS pump

Now you can achieve completely dry pressure in the 10^{-1} to 10^{-3} mm Hg range using only a *mechanical* high-vacuum pump.

Probably the world's fastest pump in this range, the new Roots pump works without the aid of oil or steam vapors.

A pair of finely machined rotary pistons do the pumping. The pistons never touch one another or the pump casing, so the Roots pump needs no oil sealing. It cannot contaminate a system with backstreaming vapors.

Consider these other advantages:

1. Speed. The model shown above has a throughput of 10,400 micron cu. ft. per minute at 10 microns.

2. No shaft seals, no leaks. Motor operates within the vacuum.

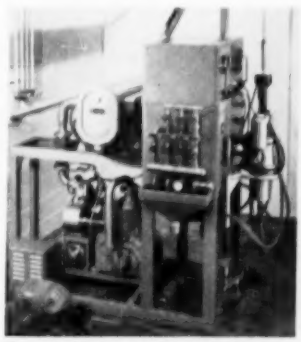
3. No by-pass or valving. Roughing is done directly *through* the pump.

4. Quiet. The Roots pump does not vibrate when in operation.

5. Low power consumption.

Under a license with the manufacturer, Heraeus (Hanau, Germany), CEC is exclusive agent for all seven models of the Roots pump in this country.

For data on performance and theory of operation, write for Bulletin P8-20.



Heraeus Vacuum Arc Melting Furnaces are also available from CEC. Note Roots pump used. Furnace melts "buttons" to ingots. Particularly useful for obtaining pure samples of metals with high melting points. Information in Bulletin P4-28.

Consolidated Electrodynamics

Rochester Division, Rochester 3, N. Y.

formerly Consolidated Vacuum

OFFICES IN PRINCIPAL CITIES THROUGHOUT THE WORLD

ISD Committee Defines Objectives in Statement

The Physical Chemistry of Steelmaking Committee, Iron and Steel Division of the Metallurgical Society of AIME, has stated its purpose and objectives.

PURPOSE

The Physical Chemistry of Steelmaking Committee shall promote the advancement of the science of iron and steelmaking and shall also be responsible for the dissemination of this knowledge in industry.

ORGANIZATION

A. Membership

All AIME members working in the field of extractive ferrous metallurgy are eligible for membership and are encouraged to participate in its activities.

B. Officers

The officers of the Committee shall consist of a chairman, a vice chairman, a secretary, and a past-chairman. A Steering Committee composed of these officers and six additional members will be responsible for directing the activities of the Physical Chemistry of Steelmaking Committee.

A Nominating Committee composed of the past-chairman and two other members appointed by the chairman will nominate the officers for the following year, a new member of the Steering Committee each year, and all new members to the Physical Chemistry of Steelmaking Committee. All nominations will be submitted to the Committee for approval.

ACTIVITIES

As part of the Committee's effort to advance the science of steelmaking, it sponsors one or more technical sessions at the Annual Meeting of the AIME, and at the National Blast Furnace, Open Hearth, and Electric Furnace Conferences. In addition, a series of regional meetings on scientific and engineering problems in steelmaking will be jointly sponsored by the Physical Chemistry of Steelmaking Committee and the various local sections of AIME.

The Physical Chemistry of Steelmaking Committee wrote *Basic Open Hearth Steelmaking* and is now writing a similar handbook on electric furnace steelmaking as part of their objective to make all recent advances in the science readily available to industry. Other activities of a similar nature will be sponsored by the Committee in the future as the necessity arises.

Abstracts Due For 1958 Nuclear Congress

Industrializing the Atom will be the theme for the 1958 Nuclear Congress now definitely set for March 17 through 21 at Chicago's International Amphitheater. With plans well underway, sessions are scheduled to cover economics, finance, future plans, and much more.

All engineers and scientists working in the nuclear field are urged to contribute one or more papers. There were 158 papers from all aspects of nuclear science and engineering at the 1957 Congress in Philadelphia. Abstracts are due by July 15, 1957, and AIME authors should get in touch immediately with Frank A. Rough, Battelle Memorial Institute, 505 King Ave., Columbus 1, Ohio. All papers are being handled by individual societies and not by Engineers Joint Council. Co-ordinated by EJC, for its member societies, managed by American Institute of Chemical Engineers, and sponsored by the engineering and scientific societies interested in the nuclear field, the 1958 Congress promises to be bigger than ever. Once again the Hot Laboratories and Equipment Conference, and the National Industrial Conference Board's Atomic Energy in Industry Conference will be part of the 1958 Nuclear Congress.

A major part of the Nuclear Congress will again be the International Atomic Exposition where engineers, scientists and management men can see and discuss with industrial representatives, all nuclear processes and materials currently available. At Philadelphia in 1957, a total of 16,429 engineers, managers and scientists attended the Exposition. With the advances a year can bring to the rapidly growing industry, the 1958 Exposition should attract more.

Under the leadership of John R. Dunning, chairman of the Nuclear Congress Policy Board, Bruce R. Prentice, chairman of the General Committee, and John W. Landis, chairman of the NESC Conference Committee, the 1958 Nuclear Congress is expected to mirror all the advances of the nuclear field. Authors are again urged to submit their proposed papers to their societies as soon as possible.

Detroit Steel Meeting

(Continued from page 809)

General Motors Corp., publicity and program chairman; Charles W. Phillips, University of Michigan, and Harry W. Clark, Ford Motor Co., program committee co-chairmen; W. E. Hart, Ford Motor Co., and M. Semchyshen, Climax Molybdenum Co., banquet committee co-chairmen; H. E. Jones, Jones Mundle & Co., and G. Sprecht, Jr., Electro Metallurgical Co., supplies committee co-chairmen.

RPI Courses Aim For An Integrated Program In Nuclear Engineering

Rensselaer Polytechnic Institute, in Troy, N. Y., has a unique approach to nuclear training. Instead of a separate department of nuclear engineering, these studies are integrated with ten other science and engineering departments. According to V. L. Parsegian, chairman of the R.P.I. Engineering Faculties, ". . . this approach will more effectively develop the large variety and number of specialists, including physicists, chemical engineers, metallurgists, etc. on whom the nuclear power industry must depend." Dr. Parsegian added, ". . . a metallurgist can make his best contribution to the nuclear field by taking his master's or doctoral degree within the department of metallurgical engineering . . . . . and combine essential non-nuclear courses with three to five courses selected from the nuclear series."

The program comprises a series of 16 graduate courses covering key technical areas of nuclear work, including introductory and advanced nuclear courses in reactor physics, metallurgy, heat transfer and thermal stress analysis, chemistry and chemical engineering, management of atomic operations, and a special key course that develops complete power reactor projects under the guidance of several instructors. A number of these courses combine laboratory experiments and lectures.

The nuclear series is flexible so that a graduate student registered in any department can select the sequence of nuclear electives to best prepare him for his future work.

There have been approximately 400 registrants for these nuclear courses during the current school year; nearly half of whom have been scientists and engineers of the Knolls Atomic Power Laboratory.

San Francisco ESPS Elections and Awards

The San Francisco Advisory Committee of the Engineering Societies Personnel Service presented a Certificate of Award to Herbert A. Sawin for his work in the field of personnel placement. Mr. Sawin, of Yuba Mfg. Co., retired from ESPS after more than 30 years of service.

The Branch announced the results of its election: chairman, Bertram S. Truett, ASME, American Meter Co.; vice chairman, Lauress L. Wise, associate editor, *Engineering News Record*; secretary, Morris Weitzner, Bethlehem Steel Co.; treasurer, Paul M. Ruedrich, Nopco Chemical Co.; assistant secretary, Bennett L. Raffin, ASCE, Rothschild, Raffin & Weirick; and assistant treasurer, L. A. Norman, AIME, Equipment Engineers.

PERSONALS

A. S. COHAN

Alvin S. Cohan, formerly assistant director of public relations and advertising, Titanium Metals Corp. of America, has joined the Public Relations Dept., J. M. Mathes Inc. Mr. Cohan is a former AIME Manager of Publications and editor of JOURNAL OF METALS.

Howard J. Luetzow, former assistant metallurgical engineer, Argonne National Laboratory, has been appointed technical sales representative for the Chicago district, Wolverine Tube Div., Calumet & Hecla Inc.

M. J. Weldon, former metallurgist at Northeastern Steel Corp., Bridgeport, Conn., has accepted a position with Henry G. Thompson & Son Co. in New Haven.

Howard J. Eyman has resigned his position with Carnegie Illinois Steel Corp., Pittsburgh, to join U. S. Steel Corp. in that city.

John W. Gardner, a member of the board of directors of Gardner-Denver Co., Quincy, Ill., has been named coordinator of new products development. He has been serving in the engineering and sales departments of the company.

J. W. GARDNER

Kenneth F. Waggener has been named assistant superintendent of the bessemer converter mill, Youngstown District, Republic Steel Corp. He has been with Republic since 1937.

At Reserve Mining Co., a joint venture of Armco Steel Corp. and Republic Steel Corp., Silver Bay, Minn., **C. L. Kingsbury** is retiring as vice president. Mr. Kingsbury, who was vice president and general manager, Rustless Iron & Steel Corp., prior to the incorporation of that company into Armco, will continue in a consulting capacity to Armco Steel Corp. **J. William Bryant,** who will assume Mr. Kingsbury's duties, has been elected a vice president. Associated with Armco for the past 33 years, he served most recently as controller and assistant treasurer in the Cleveland office.

Glenn O. Wilson has been promoted to director of the Industrial Technical Div., Dorr-Oliver Inc., Stamford, Conn. He had been serving as industrial sales manager.

W. D. JONES

William D. Jones has resigned his post as assistant director of personnel and industrial relations, National Lead Co. of Ohio, to become manager of industrial relations of the Toronto, Ohio, plant, Titanium Metals Corp. of America.

Malcolm F. Judkins, manager, New Products Div., Firth Sterling Inc., Pittsburgh, recently addressed the California State Polytechnic College student chapter of the American Soc. of Tool Engineers. His talk dealt with *Industrial Nuclear Power.*

Alaettin M. Aksoy, chief metallurgist for the Vacuum Metals Div., Crucible Steel Co. of America, Pittsburgh, addressed the National Passenger Car Body and Materials meeting of SAE on March 6. His subject was *The Effect of Vacuum Melting on Low Alloy Steels.*

R. F. Helmke, geologist for Bradley & Eckstrom Inc., is now located at 24 California St., San Francisco.

B. N. AMES

Bernard N. Ames, president of Columbian Bronze Corp., Freeport, N. Y., has joined John B. Salterini Co. Inc. as a member of the board of directors. Mr. Ames, a pioneer in the development of shell molding technology in this country, served for many years with the New York Naval Shipyard as head of the casting development and foundry practices section of the Materials Laboratory. He has received several citations from the Navy Dept. for his technical and practical work in foundry practices.

Richard N. Miller, a member of the staff of Vitro Uranium Co., Salt Lake City, since 1948, has been appointed to the new position of assistant to the president, responsible for long-range planning. He has been serving as plant engineer since 1954.

Richard P. Simmons has been promoted to manager of processing of the Toronto, Ohio, plant, Titanium Metals Corp. of America. He had been supervisor of the titanium section, Brackenridge Works, Allegheny Ludlum Steel Corp.

Donald C. Coleman is director of operations and development, Wilputte Coke Oven Div., Allied Chemical & Dye Corp., New York. He was formerly associated with U. S. Steel Corp., Fairless Hills, Pa.

D. C. COLEMAN

Richard L. Reddy, formerly of the department of metallurgical engineering, Rensselaer Polytechnic Institute, Troy, N. Y., has joined the staff of Metals Research Laboratories, Electro Metallurgical Co., Niagara Falls, N. Y.

Charles D. Coxe has been promoted from assistant manager to manager of the Metallurgical Dept., Handy & Harman. He has been associated with the New York firm since 1946.

A. L. CARROLL

In the Engineering and Construction Dept. of Electro Metallurgical Co., **A. L. Carroll** has been appointed project comptroller, while **H. S. Newhall** has become chief development engineer. Mr. Carroll has been associated with Electromet since 1955, and was responsible for the design engineering of the company's Engineering Center under construction in Niagara Falls. Mr. Newhall, who joined the department in the same year, was formerly a metallurgical and sales engineer, Lectro Furnaces Inc., a division of McGraw Electric Co.

H. S. NEWHALL

Loren W. Smith has resigned as head of the metallurgy section, Materials Dept., Cornell Aeronautical Laboratory, Buffalo, to become assistant vice president and director of metallurgical development, Symington-Gould Corp., Depew, N. Y.

B. S. LEMENT

Bernard S. Lement has been named director of research, Div. of Physical Metallurgy, Manufacturing Laboratories Inc. A former assistant professor at the University of Notre Dame, Dr. Lement was a member of the research staff of Massachusetts Institute of Technology where he received his B. S. and D.Sc. degrees in the department of metallurgy.

Charles W. Nichols, Jr., president of Nichols Engineering and Research Corp., is serving on the board of trustees of New York University. He is a member of the board of managers, Cooperative Social Settlement Society of New York, and a director of Allied Chemical and Dye Corp., Eugene Munsell & Co., and Niro Atomizer Ltd.

L. C. Hewitt has been elected vice president-research and development, Ironton Fire Brick Co. Prior to joining the company in 1955, Mr. Hewitt had been vice president and director of research for Laclede-Christy Co., St. Louis, a division of H. K. Porter Inc.

William T. Ahlborg, formerly vice president and secretary, Denver Equipment Co., Denver, has been appointed executive vice president and general manager.

W. T. AHLBORG

Cyril S. Smith has been elected to the National Academy of Sciences, the highest ranking scientific body in the U. S. Professor of metallurgy at the University of Chicago, he recently resigned his post as director of the University's Institute for the Study of Metals in order to devote his time to research in the physical structure of alloys. Dr. Smith, who has been in charge of the Institute since its formation in 1945, served as supervisor of metallurgical investigations for the Manhattan Project during World War II. **Earl A. Long,** head of the Institute's Low Temperature Laboratory, succeeds Dr. Smith as director of the Institute.

Union Carbide Nuclear Co. has announced the following promotions: **Lyman A. Bliss** has been appointed president. A graduate of Stevens Institute of Technology, Mr. Bliss joined Linde Co., a Union Carbide Corp. division, becoming vice president in 1940. In 1955 he was made vice president of Union Carbide Nuclear Co. He served on the central research committee from 1944 to 1952,

F. W. HURD

and has been associated with various nuclear activities of the corporation, including the Manhattan Project.

Frank W. Hurd has been named Director of Research. He has been associated with atomic energy work since 1943. Prior to his appointment, he had been serving as superintendent of research and development, industrial applications.

Adolph Q. Lundquist has been appointed a vice president. A member of Union Carbide's staff since 1942, Mr. Lundquist has been engaged in the production of uranium concentrate as superintendent of operations of the Rifle, Colo., plant, and later general manager of Colorado Plateau operations at Grand Junction.

O. B. J. Fraser, assistant manager, Development and Research Div., International Nickel Co. Inc., New York, was recently awarded honorary membership in the American Welding Society, for exceptional ac-

complishment in connection with the joining of nickel and nickel alloys. A former president of the Society, Mr. Fraser was the recipient of its Samuel Wylie Miller Memorial Medal in 1951. **Sidney Low**, supervising engineer, Research & Development Laboratory, Chapman Valve Mfg. Co., Indian Orchard, Mass., has been designated New England district director of the American Welding Society.

K. C. BROWNELL

Changes in the management staff were recently announced by American Smelting & Refining Co. Retiring are **Roger W. Straus,** chairman of the board, who will remain as a director, and **John C. Emison,** finance committee chairman. **Oscar S. Straus** will act as finance chairman to succeed Mr. Emison, while **Kenneth C. Brownell** has advanced to board chairman from president. **R. Worth Vaughan** has been elected president. **Forrest G. Hamrick,** the new treasurer, and **R. D. Bradford,** vice president, have been elected directors of the organization; **Kershaw Harms** will serve as a vice president.

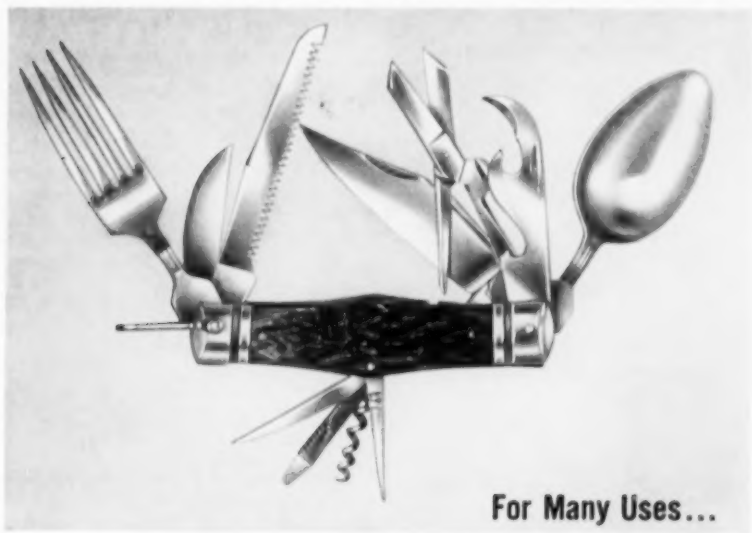
R. W. VAUGHAN

H. Glenn Rodman has been promoted to senior development engineer, Titanium Div., National Lead Co., South Amboy, N. J. He was previously development and engineering staff assistant.

Conrad F. Nagel, Jr., has retired as vice president of Aluminum Co. of America after more than 41 years of service. After two years' experience with the company, Mr. Nagel was made head of the process and products division, Technical Direction Bureau, and was named chief of the Metallurgical Dept., Fabricating Div., in 1928. He became chief metallurgist in 1944 and was elected vice president in 1952. He also has served as chairman of the technical and research policy committees. Mr. Nagel's contributions to the industry include the establishment of aluminum as a noncorrosive aircraft material and the development of a process for producing *feathered* aluminum used in explosives.

Ernest T. Weir, chairman and chief executive officer, National Steel Corp., Pittsburgh, has retired from the organization which he founded and which has been dominated by his presence for many years. He began his career in the Braddock, Pa., Wire Co. and reached the executive level at the age of 30 as president of Phillips Sheet & Tinplate Co., Clarksburg, W. Va., which grew into the Weirton Steel Co. In 1929, Mr. Weir assumed the lead in or-

(Continued on page 812B)



Especially Designed for Steel Mill Maintenance

MAX-BOND

A Super, Mouldable Refractory of Many Uses

A many-bladed knife has a multitude of uses—as everyone knows! Such a product is Mex-R-Co MAX-BOND, a specially designed refractory product for a thousand-and-one uses in keeping steel mill furnaces operating at top efficiency.

MAX-BOND is unequalled for repairing all fire clay structures — high-duty, super-duty, or high-alumina. Its mouldable characteristic makes it easy to quickly install — regardless of the location or contour. It sets up with high strength, with or without heat. MAX-BOND is economical to use because it eliminates the need for special refractory shapes. It is "Poly-wrapped" to remain consistently fresh.

Steel mills have long wanted a product for general maintenance and repair. MAX-BOND is the answer. Try it . . . avail yourself of the cost-cutting benefits of MAX-BOND Maintenance.

Write now for further information, and arrange for test installation.

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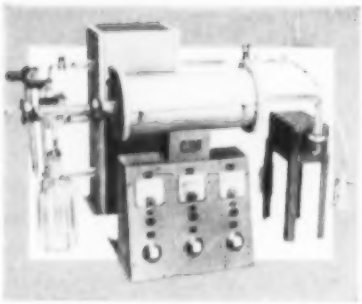

New, improved

OXYATOR

now permits **continuous operation** in the determination of Oxygen in metal

Research by Ledoux & Company has resulted in this new and advanced Model 3TG-2 Oxyator. Now for the first time, continuous operation has been made possible. This new and important feature incorporates the use of the multiple sample loading arm which permits the introduction of a new sample immediately upon the completion of the previous determination. The results are greater speed and lower costs in the determination of Oxygen in metals.

FEATURES:

* **Better Representation:** Larger samples (2 to 3 grams) are used.
* **Excellent Reproducibility**
* **Greater Speed:** Less than 2 hours per determination on most materials.
* **Simplified Operation:** With proper training, technicians can obtain accurate results.
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WRITE TODAY for descriptive literature giving complete information and price schedule.

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Personals

(Continued from page 812A)

ganizing National Steel Corp., which represented a merger of the assets of Weirton Steel, Great Lakes Steel Corp., Hanna Iron Ore Co., and Hanna Furnace Corp. He will continue to serve as director of the corporation.

John L. Lamont has become assistant manager of administration at Electro Metallurgical Co.'s research laboratories, Niagara Falls, N. Y. A graduate of Lehigh University, Mr. Lamont joined Union Carbide Corp. in 1929, advancing to research metallurgist, senior research assistant, and section leader in the Metals Research group. Co-author of a text, *Hardenability and Steel Selection*, he is also head of the Administrative Services Dept.

Robert H. Brown was recently promoted to assistant director of Alcoa Research Laboratories, Pittsburgh. Mr. Brown joined the metallurgical division of Alcoa in 1931, later transferring to the chemical metallurgical division where he was appointed chief in 1945. A pioneer in establishing the theory of cathodic protection, he was fourth in the world to receive the Whitney Award of the National Assn. of Corrosion Engineers, presented to him in 1950.

OBITUARIES

C. D. King

An Appreciation
by Walther Mathesius

Clarence David King, assistant to executive vice president-operations, U. S. Steel Corp., died in Pittsburgh on March 24, at the age of 63. With his passing came to a close a singularly distinguished career in the steel industry.

Born in Brooklyn and graduated from Yale University in 1914, he began his life-time service for U. S. Steel as a metallurgist with the Clairton, Pa., Works in the same year. In 1930 he joined the technical staff group of U. S. Steel in New York as assistant to C. A. Meissner, taking on the chairmanship of U. S. Steel's open hearth committee. To this he added, in subsequent years, the chairmanship of the Corporation's bessemer, blast furnance, coke, and rolling mill committees. In this comprehensive activity he gained the universal appreciation of his associates owing to his faultless diplomacy, keen analytical ability, unerring logic, and eminent fairness of judgment.

When the U. S. Steel Corp. of Delaware was established as a management advisory group in 1938, "Dave," as he was known among his countless friends throughout the land, moved to Pittsburgh, where he became intimately associated with this writer, then vice president-operations, for the ensuing six years. They were marked by the complete absence of misunderstanding, by closest collaboration, and a personal harmony which, I feel certain, was appreciated by us both.

As further changes in the organizational structure of U. S. Steel Corp. became effective, "Dave" became assistant vice president-engineering in 1952, and assistant to the executive vice president-operations on Feb. 2, 1956.

Beyond the realm of U. S. Steel's official family he became widely and favorably known as the author of numerous technical papers dealing with various phases of the steel industry. The clarity and grace of his presentations were exceptional, based on a thorough knowledge of his subjects and a keen understanding of their economic worth. Dave served creditably on various technical missions in both South America and Western Europe, where his experienced and competent advice was eagerly sought.

AIME will long remember him for his contributions and unselfish devotion to the Institute. In 1945, he received the Institute's Robert W. Hunt Gold Medal for the best iron and steel paper. Chairman of the ISD in 1949, he distinguished himself as the Institute's Howe Memorial Lecturer in 1954.

Dave King's host of friends realize regretfully that his remarkable career has ended. His memory will live in their high esteem, for coming generations to revere.

Clarence G. Willard (Member 1931) passed away July 30, 1956, in Denver, following a serious illness of almost a year. A recognized authority in the ore-grinding field, Mr. Willard was born in Deadwood, S. D., and received his B.S. and metallurgical engineering degrees at the South Dakota School of Mines. His first job was with Lundberg, Dorr & Wilson Co. as mill man. In 1914 he joined the Golden Reward Mining Co. at Terry, S. D., beginning as metallurgist, and later becoming master superintendent. He also did consulting work prior to his association with the Mine & Smelter Supply Co., Denver, where he was manager of the Marcy Mill Div. Subsequently, he became executive vice president and director of Colorado Iron Works Co., a division of Mine & Smelter. A member of the American Mining Congress, Mr. Willard was also active in the Colorado Mining Assn. He is survived by his wife, five children, and six grandchildren.

Frank Weir (Member 1952) died on April 23 at the age of 57, after an illness of several months. A native of Glasgow, Scotland, Mr. Weir came to the U. S. in 1923. He became asso-

ciated with Harbison-Walker Refractories Co. in 1931 and served in sales positions in New York, Boston, Buffalo, St. Louis, and Pittsburgh. He was appointed district sales manager in St. Louis in 1946, and became assistant general sales manager in 1955.

Mr. Weir was a member of the Duquesne Club, the Pittsburgh Athletic Assn., and the Chamber of Commerce. He is survived by a brother, William G. Weir of The Glen, Paget, Bermuda.

Malcolm Glen (Member 1949) died recently in Australia, his native land. He was born in Melbourne on Sept. 2, 1907, and attended the University of Melbourne where he received his Bachelor's degree in metallurgical engineering. At the time of his death he was associated with the North American Cyanamid Ltd. where he began as field engineer in 1947.

Dimitry Niconoff (Member 1940), metallurgist with Republic Steel Corp., Canton, Ohio, died Mar. 16, 1957. A native of Nicolaev, Russia, he was born on May 24, 1898, and graduated from South Dakota School of Mines with a B.S. degree in metallurgy. His metallurgical training continued at the University of Utah and Carnegie Institute of Technology. In 1928, he took his first job with United Verde Copper Co. of Clarkdale, Ariz. He joined Battelle Memorial Institute in 1936, leaving after three years to resume postgraduate study at Ohio State University, where he was awarded his doctorate in 1940. Dr. Niconoff was active in AIME, AFA, ASM, and the Electrochemical Society.

David Avery (Member 1917) died last October in his native land, Australia. Born in 1871, he received an M.S. degree in chemistry and physics from Melbourne University. Mr. Avery was head of the chemistry department, Melbourne Technical School from 1898-1910. Later he opened his own consulting office specializing in treatment of lead ores, including flotation work, byproducts, and plant economics.

Frank G. McCutcheon (Member 1955) died Mar. 27, 1957, at the age of 67. Born in Vernon County, Mo., he attended Morrisville College, receiving a B.S. degree. He began his career as a chemist at Cockerill Zinc Co. in 1909, from which position he rose to assistant superintendent, Bartlesville Zinc Co. In 1937 Mr. McCutcheon became associated with Eagle-Picher Co., where many of his most important contributions were made. Having originated techniques for producing gallium and indium, he also developed a process for removing germanium from electrolytic zinc cell solutions and went on to devise better methods for cadmium recovery and retort zinc smelting, during his service with the company. The former technical director of Eagle-Picher's Mining & Smelting Div. co-authored an AIME technical publication, *Effects of Length of Cycle on the Economics of Retort Smelting*, and an article on cadmium for a recent book on rare metals.

NECROLOGY

Date Elected	Name	Date of Death
1943	Allan E. Craig	April 7, 1957
1920	J. S. Hazen	Feb 13, 1957
1955	Frank G. McCutcheon	Mar 27, 1957
1940	Dimitry Niconoff	Mar 16, 1957
1952	Howard R. Youngkrantz	Mar 27, 1957

MEMBERSHIP

Proposed for Membership
Metallurgical Society of AIME

Total AIME membership on Apr. 30, 1957, was 27,129; in addition 2,849 Student Associates were enrolled.

ADMISSIONS COMMITTEE

Harold K. Work, Chairman; Francis B. Foley, T. D. Jones; E. S. Machlin; J. H. Scaff; Paul Von Stein; T. B. Winkler.

The Institute desires to extend its privileges to every person to whom it can be of service, but does not desire as members persons who are unqualified. Institute members are urged to review this list as soon as possible and immediately to inform the Secretary's office if names of people are found who are known to be unqualified for AIME membership.

Members

John Quincy Adams, Whittier, Calif.
G. William Bauer, Warren, Ohio
Raymond C. Bell, Rossland, B. C., Canada
DeSpence Bentley, Tampa, Fla.
A. Berghezan, Brussels, Belgium
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COMING EVENTS

June 7, AIME, NOHC Southern Ohio Local Section, annual golf party, Middletown, Ohio.

June 10, AIME, NOHC Pittsburgh Local Section, golf party-meeting, Short Hills Country Club, Pittsburgh.

June 16-21, ASTM, annual meeting, Chalfonte-Haddon Hall, Atlantic City, N. J.

June 28, AIME, NOHC Eastern Section, golf party, Coatesville Country Club, Coatesville, Pa.

Sept. 8-Oct. 9, Commonwealth Mining and Metallurgical Congress, British Columbia to Nova Scotia.

Sept. 13, AIME St. Louis Section, joint meeting with Amer. Chemical Soc. St. Louis Section, Hotel York, St. Louis.

Oct. 3-4, AIME, NOHC Southwestern Local Section, fall meeting, Shamrock Hotel, Houston.

Oct. 6-10, Electrochemical Soc., Statler Hotel, Buffalo.

Oct. 9-11, Joint Solid Fuels Conference, ASME-AIME Coal Div., Chateau Frontenac, Quebec.

Oct. 11, AIME, NOHC Eastern Local Section, 11th annual technical meeting, Sheraton Hotel, Philadelphia.

Oct. 18-19, AIME, NOHC Southern Ohio Local Section, annual meeting, Deshler-Hilton Hotel, Columbus, Ohio.

Oct. 30-Nov. 1, AIME Rocky Mountain Minerals Conference, Denver.

Nov. 1, AIME Pittsburgh Section and NOHC Pittsburgh Section, 12th annual Off-the-Record Meeting, Penn-Sheraton Hotel, Pittsburgh.

Nov. 2-8, Second World Metallurgical Congress, Chicago.

Nov. 4-7, AIME, IMD Fall Meeting, Morrison Hotel, Chicago.

Nov. 12, AIME, NOHC Buffalo Local Section, annual meeting, Royal Connaught Hotel, Hamilton, Ont., Canada.

Dec. 4-6, AIME, 15th Electric Furnace Steel Conference, Penn-Sheraton Hotel, Pittsburgh.

Feb. 16-20, 1958, AIME Annual Meeting, Statler and Sheraton-McAlpin Hotels, New York.

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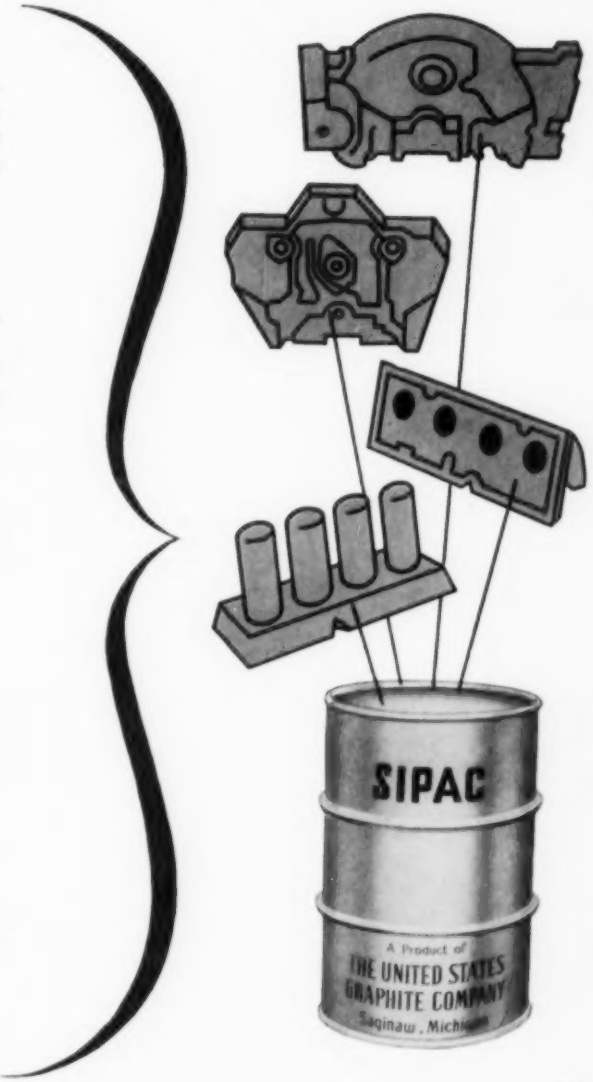

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